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Electron Spectroscopy and the Study of Chemical Reactions on the Surfaces of Metals

A.G.Akimov and L.P.Kazanskii

The experimental technique and the physical principles of the fundamental electron spectroscopic methods are examined: X-ray electron spectroscopy (XES), Auger electron spectroscopy (AES), and ultraviolet photoelectron spectroscopy (UPES). Their advantages and disadvantages are compared. The application of electron spectroscopic methods in the study of chemical reactions on the surfaces of metals is considered in relation to the investigation of the oxidation of metals and alloys in both the vapour-gas phase and in aqueous electrolytes. In addition, studies on the application of XES and AES to the investigation of corrosion processes at the metal-electrolyte interface are discussed.
The bibliography includes 76 references.

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I. INTRODUCTION

The chemical reactions occurring on the surfaces of solids have been the subject of studies in many independent branches of physical chemistry† such as catalysis, electrochemistry, metal corrosion, etc. As a rule, the interaction of the surface of a solid with the components of the surrounding medium involves a chemical modification of the surface itself. Investigation of such "modification" by methods of electron spectroscopy makes it possible to obtain qualitative and quantitative information about the nature of the interactions on the surface of the solid, which range from adsorption interaction to a significant alteration of the chemical composition of a surface region with a thickness up to 10^{-5}–10^{-4} cm.

The set of methods referred to as "electron spectroscopy" includes X-ray electron spectroscopy (XES)#, Auger electron spectroscopy (AES), ultraviolet photoelectron spectroscopy (UPES), the spectroscopy of characteristic losses (SCL) (or electron energy loss spectroscopy), and many other methods.

†The techniques for the physicochemical study of chemical reactions on the surface is considered in A.Adamson's monograph "The Physical Chemistry of Surfaces" (Translated into Russian), Izd.Mir, Moscow, 1979.

#This method has been referred to as ESCA (electronic spectroscopy for chemical analysis) by the authors—a team of Swedish scientists working under the supervision of K.Siegbahn[1].

This review deals mainly with the first three methods, since they have found most extensive applications in studies on the chemical composition of the surfaces of solids. A common feature of all the methods under consideration is that the spectrum of electrons is subjected to final analysis. The physical principles of the excitation of the spectrum of electrons are described in the next section.

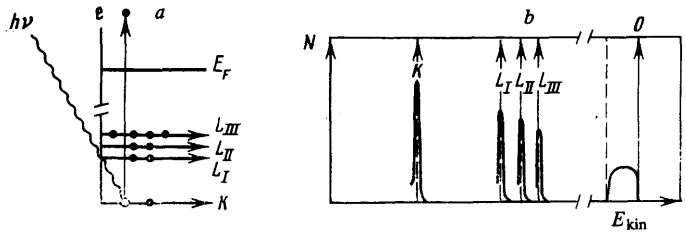


Figure 1. Schematic illustration of the electronic levels in a metal with ionisation of the K level (a) and the corresponding electron spectrum[1] (b): E_F = Fermi level; e = free electron; N = number of photoelectrons; E_b = binding energy of electrons; E_{kin} = kinetic energy of photoelectrons.

II. PHYSICAL PRINCIPLES AND ANALYTICAL POSSIBILITIES OF ELECTRON SPECTROSCOPIC METHODS

Fig. 1a [1] illustrates the diagrams of electronic levels in a metal. The action of a quantum of known energy on the K shell leads to its ionisation; if the energy of the electrons is sufficiently high, the latter leave the metal and become free. By detecting the free electrons emerging from the metal under the influence of radiation, it is possible to obtain the electron spectrum illustrated in Fig. 1b. Evidently the electron spectrum corresponds to the energy level diagram in Fig. 1a. The accuracy of the measurement of the energy of the free electron is determined by the natural width of the ionised level and the accuracy of the measurement of the wavelength of the incident radiation. The spectrum illustrated in Fig. 1b is also referred to as the photoelectron spectrum and is the main object of study in XES and UPES, in contrast to the spectra of Auger electrons obtained in AES.

The mechanism of the formation of Auger electrons can be described as follows. When a vacancy is produced in one of the inner electronic levels due to its ionisation under the influence of a particular type of radiation, there is also a possibility of another type of emergence of an electron from the solid. Such a vacancy can be filled by an electron in one of the outer levels and the energy of this transition can be evolved in the form of a quantum of electromagnetic radiation or can be transferred to one of the electrons in the outer

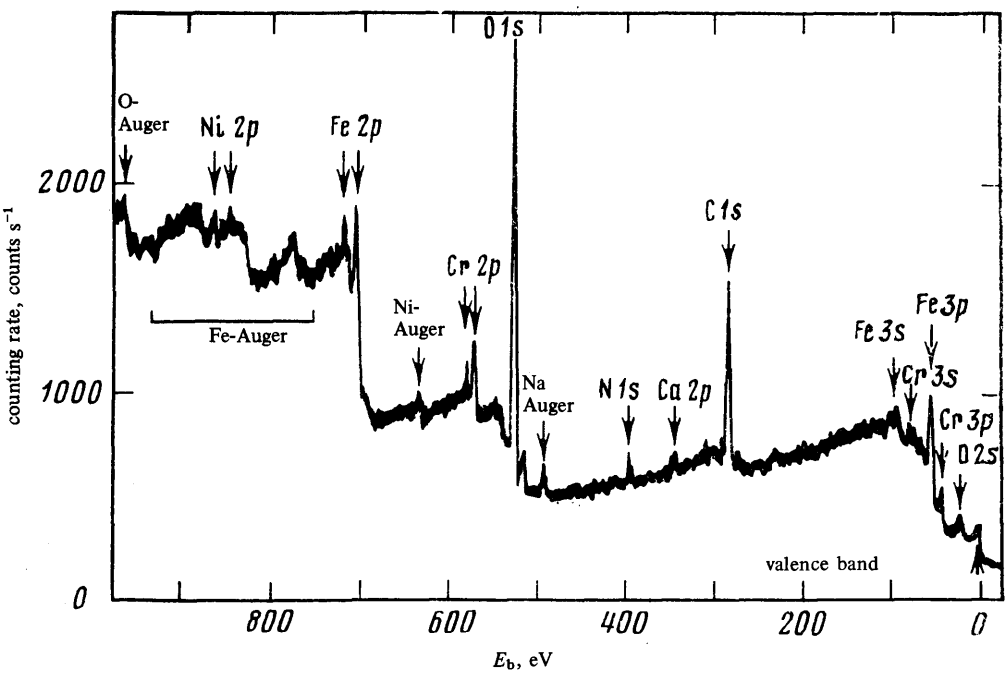


Figure 2. Electron spectrum of the surface of the Kh18N10T steel oxidised in air at 20 °C.[4]

levels, which is then ejected from the specimens. This process is referred to as the Auger effect and the ejected electrons are called Auger electrons§. The probability of the Auger process increases with decrease of the atomic number of the element, while the yield of X-ray fluorescence diminishes with decrease of the atomic number of the element. Because of this, it is possible to investigate, by analysing the spectra of Auger electrons, the surfaces of solids in order to detect light elements on the latter.

Thus, when ionising radiation acts on a metal surface, it is possible to obtain both photoelectron spectra associated with a simple one-electron process and Auger spectra associated with many-electron transitions. However, the approaches used in the analysis of the electron spectra (of both photoelectrons and Auger electrons) are very similar.

Indeed the fundamental equation of the external photoeffect is the Einstein equation:

$$h\nu = E_f - E_i + E_{kin}, \quad (1)$$

where $h\nu$ is the energy of the photons, E_f the energy of the system in the final state after the ejection of an electron from the K shell, E_i the overall initial energy of the atom or the molecule, and E_{kin} the kinetic energy of the dislodged electron. By defining the binding energy of the electrons E_b^F as the energy necessary to remove the electron from the K level to infinity (where $E_{kin} = 0$), it is possible to formulate Eqn.(1) as follows:

$$E_b^f = h\nu - E_{kin} - \varphi, \quad (2)$$

where E_b^F is the binding energy of the electrons of the metallic specimen measured relative to the Fermi level of the spectrometer and ϕ is the electron work function of the metal of the spectrometer. The equation relating the kinetic energy of the Auger electrons E'_{kin} to the energies of the levels of the given element is[2]

$$E'_{kin} = E_K - E_L - E_L^{z+1}; \quad (3)$$

where $E_{K(L)}$ is the energy of the $K(L)$ level of the element under consideration and E_L^{z+1} is the energy of the L level of the element having an atomic number one greater than the element of the specimen.

The determination of E_b permits the elemental analysis of the specimens, because there is a specific energy spectrum of electronic levels corresponding to each element. Fig.2 [4] illustrates the electronic spectrum obtained on irradiation of the surface of the Kh18N10T alloy oxidised in air at room temperature; the aluminium K_α line was used to obtain the X-radiation. It follows from Fig.2 that the electronic spectrum exhibits lines corresponding to photoelectrons and Auger electrons. Examination of the energies of the lines permits a qualitative analysis of the surface layer¶. The first studies by Siegbahn et al.[1] showed that the energies of the X-ray electron and Auger electron lines depend on the oxidation state of the atom of the test element. As a rule an increase of the degree of oxidation increases the shift of the binding energy of the electron (ΔE_b) relative to E_b in the zero oxidation state. Consequently, one can infer not only the elemental composition of the surface of metals but also the oxidation state of the elements. This can be illustrated by the data in Fig.3,[1] which illustrates the X-ray electron spectra of the beryllium 1s line. A structure consisting of two peaks corresponds to beryllium sputtered *in vacuo* (Fig.3*a*). According to the XES theory[1-3], the low-energy (relative to E_b) peak should be attributed to metallic beryllium and the high-energy peak is due to beryllium oxide BeO. Evidently the X-ray electron spectrum of beryllium oxidised at a high temperature (Fig.3*b*) contains only the high-energy peak, which confirms the validity of the assignment of this peak to beryllium in the +2 oxidation state.

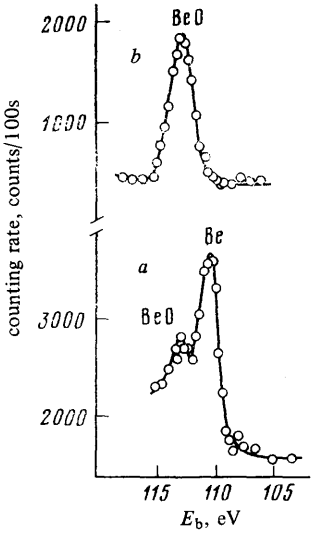


Figure 3. Electron spectra of beryllium[1] obtained by vacuum vaporisation after reduction with zirconium (*a*) and of the specimen after heat treatment in air (*b*).

It is noteworthy that the X-ray electron spectra† can carry information relating not only to the nature of the atom under investigation itself but also to its environment. A change in the charge distribution in the valence shell, occurring when the valence state of the atom is altered, influences also all the inner electrons and is therefore manifested in the electron spectra. This situation can be illustrated by the spectra of beryllium and its compounds shown in Fig.4.[1] Evidently, when beryllium is oxidised, E_b for the inner 1s electron of beryllium increases by 2.9 eV. Beryllium in BeF_2 has an even higher positive charge than in BeO [although the oxidation state is the same (+2)] as a result of the high electronegativity of fluorine, since the binding energy of the 1s electrons of beryllium in BeF_2 is greater than in BeO. In the general case the chemical shifts of the maxima in the X-ray electron spectra increase with increase of the amount of ionic character of the bond.

§For a more detailed description of the physical principles of the Auger process, see "Methods for the Analysis of Surfaces" (Edited by A.Zaderna) (Translated into Russian), Izd.Mir, Moscow, 1979.

¶Problems concerning the thickness of this layer will be considered below.

†Only the information obtained from the XES is considered, since allowance for the effects of collective interactions is extremely difficult for the two-electron Auger process.

In compounds where the test element exists in different oxidation states but is surrounded by identical atoms E_b varies approximately linearly with the degree of oxidation, which has been shown[3] in relation to nitrogen and chlorine oxides.

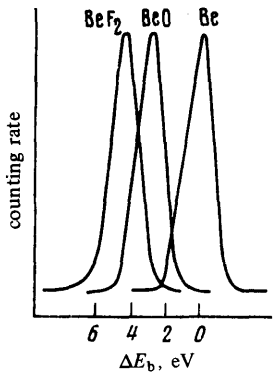


Figure 4. The positions of the lines due to metallic beryllium, beryllium oxide, and beryllium fluoride in the electron spectrum[1]; ΔE_b = change in binding energy.

For elements of a single Period, the line shift in the electron spectrum varies linearly with the total number of valence electrons and with the formal degree of oxidation[5,6].

According to the estimates of Siegbahn et al.[1], the photoelectrons abstracted from the surface carry information about a surface layer not thicker than 100 Å. Later studies showed that this layer can be even thinner. Thus the investigation of gold coated by a thin layer of graphite showed[7] that, when the electron energy changes from 1169 to 920 eV, the thickness of the layer of graphite which absorbs 95% of the electrons changes from 55 to 43 Å. By selecting the energy of the exciting radiation, E_b, and the angle of the path of the electrons between the surface and the spectrometer slit, it is possible to increase the thickness of the layer investigated to ~10 Å.[3] Fraser et al.[8] arrived at the same figure by considering the mean free path of the electron in non-elastic scattering in close-packed solids. According to Nemoshkalenko and Aleshin[2], when the energies of the primary electrons are suitably selected, AES can carry information about 2–3 monolayers of the test substance.

We shall consider the scope of the quantitative analysis by electron spectroscopy. The data given below refer to photoelectron spectra and primarily to XES, since a complete quantitative theory of analysis with the aid of AES is still being established.

Having assumed that the intensity of the beam of X-ray photons does not undergo appreciable changes in the surface region 100 Å thick, the intensity I of a stream of photo electrons with a specified energy can be expressed[2] by

$$dI = F\sigma Nk \exp(-x/\lambda)\,dx, \qquad (4)$$

where F is the intensity of the stream of X-ray photons, σ the photoionisation cross-section for the given energy of the photons and the atomic level under consideration, N the number of electrons of the given kind per unit volume of the substance, k the constant for the given spectrometer, x the distance which the electron traverses in the substance, and λ the effective depth from which electrons emerge, determined by the length of the free path of the electron in the test substance.

Using Eqn.(4), the following expression can be written for the intensity of the stream of photoelectrons which have emerged from a massive specimen:

$$I = F\sigma_1 N_1 k\lambda_1 [1 - \exp(-d/\lambda_1)], \qquad (5)$$

where d is the thickness of the layer which the photoelectrons have traversed. It follows from Eqn.(5) that the intensity is linearly related to the number of atoms in the test substance N_1 and this constitutes a basis of the quantitative analysis. Indeed, using Eqn.(5) to determine the relative increments in the concentrations of the components of the surface, the following simple expression can be obtained when the λ_i of the components are equal:

$$I_A/I_B = \sigma_A N_A (\sigma_B N_B)^{-1}. \qquad (6)$$

Here subscripts A and B refer to components A and B. The values of σ are known for virtually all chemical elements from the results of a number of studies[9,10]; although the accuracy of the tabulated σ is low (~10%), the availability of known values of σ makes it possible to employ Eqn.(6) and hence XES for quantitative analysis. One should not forget that Eqn.(6) was derived taking into account a number of simplifying postulates and therefore in each specific case one must estimate its applicability.

A more rigorous theory of photoelectron emission[11], developed taking into account the difference between the probabilities of excitation from states with different symmetries and the differences between the effects associated with the scattering of the electron wave in the crystal and on its surface, leads to much more complex expressions than Eqns.(4)–(6). However, practical experience has shown that the use of Eqns.(4)–(6) is in most cases justified.

In applying the XES method to quantitative analysis, one should remember that the existing apparatus has a maximum absolute sensitivity of ~10^{-10} g.[12,13] However, the relative sensitivity of the XES method does not exceed ~0.1% and it is therefore irrational to employ, for example, XES when the content of the given alloy component on the surface is less than 1% relative to the base.

It is of interest to compare the XES, UPES, and AES methods. The fundamental advantages of the UPES method are shown in the study of the changes of the energies of the electronic levels close to the valence band. This is due to the comparatively small range of the energies of the emitted electrons associated with the comparatively low energy of the exciting light quanta when a helium discharge lamp is used as the source of radiation. At the same time, the resolution of the UPES method can be to within 0.05 eV, which is more than an order of magnitude better than the resolution of the best X-ray electronic spectrometers. This feature of the UPES makes it possible to investigate fine effects such as the change in the structure of the valence band following a change in the concentration of one of the alloy components or the role of π,σ interactions in the adsorption of molecules, including hydrocarbons[14], on the surfaces of metals. The possibilities of UPES in the study of surfaces have been described in greater detail in another review[15].

It follows from Eqn.(3) that the measurements of the kinetic energies of the Auger electrons of atoms in different compounds should yield virtually the same information about the nature of the chemical bond as the values of E_b. In certain cases the Auger spectra have a definite advantage over the photoelectron spectra. In particular, the depth from which electrons in the substance emerge depends on the kinetic energy of the electron; therefore, knowing the distribution

of Auger electrons, it is possible to estimate the thickness of the surface layer investigated. The shift of the lines due to Auger electrons can be greater than the shift of the line due to photoelectrons[16]. Furthermore, owing to the greater efficiency of the liberation of the Auger electron and the possibility of creating fairly powerful beams of primary exciting electrons, the rate of accumulation of Auger spectra can exceed by a factor of 10^2 the rate of accumulation of X-ray electron spectra. However, a number of studies have shown that the effect of a beam of primary electrons can lead to a series of irreversible changes in the surface. These effects are associated both with the desorption of the adsorbed molecules from the surface under the influence of the electron beam[17] and with the surface dissociation and subsequent diffusion of the components of the specimen into the bulk of the specimen[18]. A recent detailed analysis of the "beam effects"[19] enabled the authors to conclude that the AES should be used as an auxiliary method in the quantitative study of the surface. AES should then naturally be regarded as an extremely effective means of the elemental analysis of the surface.

Compared with the excitation of the spectrum by a beam of electrons, used in Auger spectroscopy at the present time, the excitation by X-ray quanta is characterised by smaller cross-sections of the desorption of the adsorbed substances and a weaker secondary electron background. The relatively small intrinsic width of the lines due to the photoelectrons emitted from the inner shells greatly improves the accuracy of the measurement of the "chemical shift" of the spectral lines. The interpretation of the spectra of inner electrons is simpler than that of the results of the many-electron Auger process. The sensitivity of the photoelectron spectra excited by X-rays to substances adsorbed on the surface can be increased by selecting the corresponding angles between the ejected electrons and the surface of the specimen[20].

In many instances it is possible to achieve a sensitivity equivalent to ~0.01 of the monolayer in the study of adsorption by XES. Such sensitivity has been reached in practice in the study of the adsorption of CO, CO_2, and O_2 on platinum[13]. A direct comparison of the sensitivity of the XES (ESCA) and AES methods has been carried out in a study[21] where X-ray electronic and Auger spectra of 54 elements (ranging from lithium as the lightest element to technetium as the heaviest element) were obtained under the same conditions on the same specimens. The sensitivities of the methods were compared[21] in terms of the signal/noise ratio under the optimum conditions for the detection of the element. The results of the above study showed that the XES method is more sensitive for 10 elements (Na, Cr, Mn, Kr, Cd, Sb, Xe, W, and Th), while for the remainder the AES method is more sensitive.

Thus the XES method is at present the most universal for analytical purposes. On the other hand, in the study of each specific object one should bear in mind the advantages and disadvantages of each of the methods described and, in investigating an object which had not been studied previously, it may prove extremely useful to compare the Auger and photoelectron spectra.

III. EXPERIMENTAL TECHNIQUE

The fundamental design of the electron spectrometer used to obtain electron spectra, which is involved in virtually all modern models of electron spectrometers, combines all three methods: UPES, AES, and XES. The presence of three excitation sources makes it possible to obtain with the maximum efficiency the electron spectra considered in these methods, while a single system can be used to detect the electrons.

Ultraviolet light and X-ray generators and electron guns are used as sources of exciting radiation. Ultraviolet light is generated mainly by capillary discharge lamps filled with helium at a pressure of ~1 mmHg. The resonance line at a wavelength of 584 Å (21.21 eV) predominates in the discharge. The emission is collimated with the aid of a capillary tube. The sources of X-rays consist of both the usual X-ray tubes and of tubes with a rotating anode (to decrease the local over-heating of the anode). The material of the anode is usually aluminium and magnesium and rarely copper and chromium. The radiation is made monochromatic to increase the resolution of the spectrometers.

In modern X-ray spectrometers there are two types of analysers: magnetic and electrostatic. In magnetic spectrometers the electrons are focussed with the aid of a magnetic field. Apparatus with double magnetic focussing has been described[1]. In almost all commercial spectrometers electrostatic focussing is used nowadays; in this case the requirements for the compensation of the Earth's magnetic field are much less stringent. The scanning of the spectrum with respect to energy is achieved by a retarding electrostatic field applied as a rule between the spectrometer and the source. In the best modern electron spectrometers provision is made for highly efficient systems designed to generate an ultrahigh vacuum. The residual pressure after evacuation with heating at ~200° is $\sim 10^{-10}$ mmHg. The maximum pressure of the gas (vapour) in the specimen chamber depends on the excitation source employed but does not exceed 10^{-5} mmHg.

After passing through the analyser, the electrons are detected by a radiation receiver. In the first spectrometers of Siegbahn's group[1] photographic plates were used for detection. Nowadays electrons are counted with the aid of proportional counters or electron multipliers.

Although the fundamental design of the electron spectrometers has not changed, the measuring technique continues to improve. Thus a method has been described[22] for eliminating the interfering background signal which is superimposed on the Auger spectra in the region of low electron energies and depends strongly on the energy. The method consists in modulating the intensity of the electron beam with a continuous alteration of the modulation amplitude as the electron energy is varied, which causes a corresponding change in the sensitivity of the spectrometer as a function of the energy. This method made it possible to detect many intense closely spaced peaks for low electron energies, i.e. under conditions where the fine structure is usually lost.

One should note that in the industrial production of electron spectrometers a tendency has arisen very recently to manufacture two types of instruments. The first type consists of high-speed spectrometers designed for the rapid analysis of several specimens immersed in the vacuum chamber simultaneously (sometimes up to 20), which can consist of a combination of two complex instruments. Thus "Physical Electronics Industrials"# has manufactured an instrument which is a combination of X-ray electron and scanning Auger spectrometers; 12 specimens can be fixed simultaneously in the cassette of the apparatus. However, despite its considerable analytical possibilities, this device, designed for large series of routine measurements (necessary, for example, in the manufacture of the elements of integrated circuits), cannot replace the instruments of the second type, designed for scientific research. In these instruments (for example, in the ESCA-3 electron spectrometer)[2] the time required to obtain the spectra of a series of specimens is much longer.

#See "Handbook for Electron Spectroscopy", PEI, N.Y., 1978.

However, the instrument has a chamber for the preliminary treatment of the specimen, separated from the analyser chamber by a vacuum lock. In this device the metallic specimen can be etched by an ion beam in order to obtain a clean surface. The specimen can be heated (using an electron gun) to 1800 °C or cooled to the temperature of liquid nitrogen. In the preliminary treatment chamber the metal can be sputtered. The provision of metering taps in the chamber makes it possible to treat the specimen in a specified atmosphere. The content of the components of the atmosphere is controlled by a quadrupole mass-spectrometer, the sensor of which is mounted directly in the preliminary treatment chamber. This auxiliary equipment significantly extends the scope of the experiment.

IV. OXIDATION OF METALS

The oxidation of metals, particularly at temperatures close to 300 K, which leads to the formation of very thin oxide films, is one of the most "natural" processes investigated with the aid of electron spectroscopy. This is why the first studies on the oxide films on metals, arising when oxygen interacts with the surface, were carried out almost simultaneously with the development of the method of electron spectroscopy itself[1]. The early studies of the oxidation of metal surfaces have been briefly reviewed[3,23]. We shall examine below the fundamental results of a series of investigations which not only made it possible to understand more deeply the mechanism of the initial stages of the oxidation but also in many instances led to the discovery of hitherto unknown effects.

The considerable practical value of iron and its alloys have apparently been the cause of the extensive research carried out in different countries into oxidised surfaces of iron (and iron alloys) with the aid of XES and AES. In the first study where XES was used to investigate the oxidation of iron in atmospheres of oxygen and water vapour[24] it was shown that the shift of the Fe $2p_{3/2}$ level, observed in the oxidation of iron by oxygen, depends significantly on the duration of exposure to oxygen and the pressure of the latter. The range of oxygen pressures was 10^{-2}–10^{2} mmHg. Shifts of the binding energy (ΔE_b) of the electrons of the Fe $2p_{3/2}$ level of 3.2 and 4.2 eV corresponded to the minimum and maximum pressures respectively. These results[24] show that, depending on the oxidant pressure, the relative contents of Fe^{2+} and Fe^{3+} ions in the surface layer of the oxide can be significantly altered.

On the other hand, the presence of two states of oxygen on the iron surface has been observed[24] (the O 1*s* line consisted of two peaks); the relative contribution of each state also depends on the oxygen pressure and the duration of exposure. The authors[24] explained the existence of a doublet in the structure of the O 1*s* line by the presence on the surface of two forms of oxygen—in the chemisorbed state and the form corresponding to the oxygen in the iron oxide. The latest conclusions by the above investigators[24] are in clear conflict with the results of a study[25] where it was observed with the aid of AES that, for nearly monolayer coverages, the oxygen forms with the surface bonds analogous to those in Fe_2O_3 and the "chemisorption" component of oxygen is therefore negligibly small.

The combination of AES with mass spectrometry[26] and slow-electron diffraction[7] yields extremely important information about the interaction of the surfaces of an iron single crystal with oxygen and water vapour in the very initial stages. But it has been shown[27] that the oxidation of the (100) and (110) faces leads to an increase of the lattice parameters and to a change of symmetry from cubic to hexagonal. It has been noted[26] that, for surface coverages less than a monolayer, the adhesion coefficient is close to 0.2. This quantity persists up to the accumulation of oxygen on the surface in an amount of $\sim 1.6 \times 10^{15}$ cm^2. This quantity of oxygen corresponds satisfactorily to the surface density of the Fe atoms on the (110) face. Next the adhesion coefficient falls to less than 10^{-2}. These data are correlated with the results of a study[28] where it was shown that the oxygen adsorbed on the iron surface (the oxygen–surface bond energy is 9 kcal mol^{-1}) gives rise to a surface superstructure, which leads in its turn to a sharp decrease of the adhesion coefficient. On saturation with oxygen, this superstructure rearranges to two-dimensional FeO crystals. Further adsorption of oxygen leads to the formation of a three-dimensional oxide film. An equally detailed study of the oxidation of iron by water vapour was made by Dwyer et al.[29] In determining the kinetic parameters of the adsorption of oxidant molecules on iron, the authors of the above studies did not consider the kinetics of the growth of the three-dimensional oxide. Such a study with the aid of XES was made by Akimov et al.[30], who investigated the oxidation of polycrystalline iron in oxygen and water vapour; the range of oxidant pressures was 10^{-5}–10^{-7} mmHg. Much attention has been devoted to the purity of the initial surface and the oxidants§. The purity of the oxygen and water vapour was followed with the aid of a quadrupole mass-spectrometer combined with the preliminary treatment chamber of the X-ray electron spectrometer. A gun for the etching of the surface of the specimen with Ar^+ ions was mounted on this chamber. The surface of the specimen was regarded as "clean" when the ratio of the integral intensities of the iron and oxygen signals was ~100. Approximate calculation showed that this intensity ratio corresponds to the adsorption of ~0.1 of a monolayer of oxygen on the surface. Figs.5*a* and 5*b* [30] present the X-ray electron spectra of the Fe $2p_{3/2}$ lines for oxidation with oxygen and water vapour. Figs.5*c* and 5*d* illustrate the X-ray electron spectra of the O 1*s* line also for oxidation with oxygen and water vapour respectively. Analysis of the data presented in Fig.5 permitted the following conclusions.

1. After exposure of iron to oxygen (duration of exposure ≥ 10 *L*¶), an oxide film having the composition Fe_3O_4 is formed on its surface. This conclusion is based on the measurement of ΔE_b for the Fe $2p_{3/2}$ line in the oxidation process, which amounted to -3.6 ± 0.1 eV, and on the stoichiometric ratio Fe/O, calculated from measurements of the integral intensities of the Fe $2p_{3/2}$ and O 1*s* lines. For comparison, one should note that ΔE_b amounts to 4.2 and ~1.0 eV for Fe_2O_3 and FeO respectively. The smaller value of ΔE_b for Fe_3O_4 compared with Fe_2O_3 is associated with the presence of iron ions in the +2 oxidation state. Ertl and Wandelt arrived at the same conclusion[32].

2. The exposure of iron to water vapour does not lead to the formation of a three-dimensional oxide film on the iron surface, as shown by the comparatively small changes in the intensity of the Fe $2p_{3/2}$ line (Fig.5*b*) and the absence of the oxide component of this line.

3. The symmetry of the O 1*s* peak, its small half-width, and the value of E_b for the oxidation of iron with oxygen show that the oxygen adsorbed on the iron immediately forms bonds analogous to the Fe–O bonds in the oxide. The clear asymmetry of the O 1*s* peak in the oxidation of iron by water vapour and the results of the Fourier resolution of this peak

§It has been shown[31] that the presence of impurities on the surface can inhibit (sulphur) or significantly accelerate (carbon) the oxidation.

¶Here *L* denotes a Langmuir (10^{-6} mmHg s).

show that oxygen exists on the surface in two states: the oxygen involved in the Fe–O bond on the surface oxide and the oxygen of the hydroxide ion—the high-energy component of the O 1s doublet.

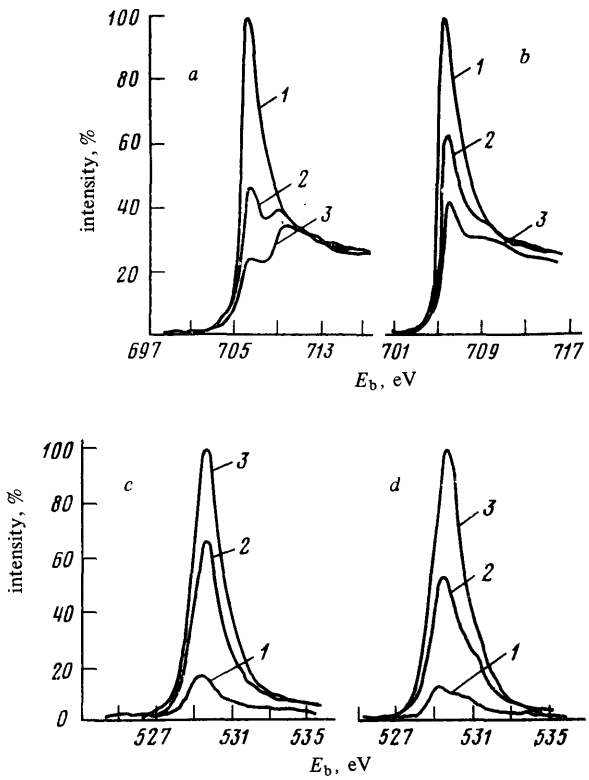


Figure 5. X-Ray electron spectra of the Fe $2p_{3/2}$ (*a* and *b*) and O 1*s* (*c* and *d*) lines for the Fe + O_2 (*a* and *c*) and Fe + H_2O (vapour) (*b* and *d*) systems; exposure (in Langmuirs): 1*a*)–1*d*) 0; 2*a*) and 2*c*) 5; 2*b*) 2.4×10^4; 2*d*) 2.4×10^3; 3*a*) and 3*c*) 10^3; 3*b*) 5×10^4; 3*d*) 5×10^3.

By analysing the dependence of the intensities of the X-ray electron lines of the elements on the duration of exposure in an atmosphere of the oxidant, it was possible to establish[30] certain kinetic relations for the initial stages of the interaction of iron with oxygen and water vapour. In the initial stage of the oxidation, where the peak in the X-ray electron spectrum of the Fe $2p_{3/2}$ line, corresponding to iron in the oxidised state, is not visible because it is overlapped by a high-intensity background caused by the scattering of the electrons dislodged from the Fe $2p_{3/2}$ level, it is difficult to infer the growth of the oxide film from the decrease of the intensity of the Fe $2p_{3/2}$ peak. Its intensity depends on the thickness of the surface film, in the given case an oxide, in the following manner[2]:

$$I=I_0\exp[-d/(\lambda\cos\alpha)], \qquad (7)$$

where α is the angle between the normal to the plane of the specimen and the spectrometer slit, I the intensity of the Fe $2p_{3/2}$ line for a given exposure, I_0 the intensity of the signal due to the clean surface, d the thickness of the film, and $\lambda = 15$ Å the depth from which electrons are emitted with a given kinetic energy[33]. Eqn.(7) is valid when the values of λ for the clean and oxidised metal surfaces are constant, which can be assumed to a first approximation.

The dependence of the thickness of the oxide film d on the duration of exposure to O_2, calculated from Eqn.(7), is illustrated in Fig.6.[30] It follows from the data in Fig.6 that, up to a thickness of ~5 Å, the oxide film grows in accordance with a linear law; for greater thicknesses, a logarithmic law governs the growth of the oxide film, corresponding formally to the model of the growth of the oxide surface put forward by Hauffe and Ilschner[23]. This shows that the transfer of charged species in the surface oxide begins to limit the rate of growth of the oxide only after the attainment of a film thickness of ~5 Å, which corresponds to two oxide monolayers.

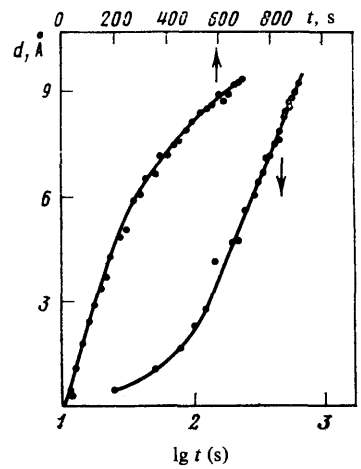


Figure 6. Dependence of the oxide film thickness (d) on the time of exposure t of iron to O_2.

The slight changes in the intensity of the Fe $2p_{3/2}$ peak following the absorption of H_2O vapour on the surface of the specimen (Fig.5*b*) suggest that this entails only the absorption of the products of the interaction between the adsorbate and the adsorbent. The degree of the adsorbent surface coverage θ can be estimated by modifying Eqn.(7) somewhat. If the thickness of the adsorbed layer does not change with θ, the modified equation relating the intensity of the Fe $2p_{3/2}$ peak to θ, can be written thus:

$$I=I_0(1-\theta)+I_0\theta\exp(-\Delta/\lambda). \qquad (8)$$

where Δ is the thickness of the adsorbed layer. On the basis of the known radii of the O^- and OH^- ions as well as the geometrical structure of the H_2O molecule, one can adopt $\Delta \cong 2.5$ Å. Having adopted, as before, $\lambda = 15$ Å, we obtain

$$I=I_0(1-\theta+0.85\theta)=I_0(1-0.15\theta), \qquad (9)$$

whence

$$\theta=6.7(1-I/I_0). \qquad (10)$$

The dependence of θ on the duration of exposure of the specimen to water vapour, calculated from Eqn.(10) for a water vapour pressure of 10^{-8} mmHg, is presented in Fig.7.[30] An estimate of the contamination of the surface by O, C, N,

and Ar atoms after bombarding it with a stream of Ar^+ ions leads to an initial surface coverage $\theta_i < 0.1$. This value of θ_i was adopted as the starting point for the θ readings in Fig.7.

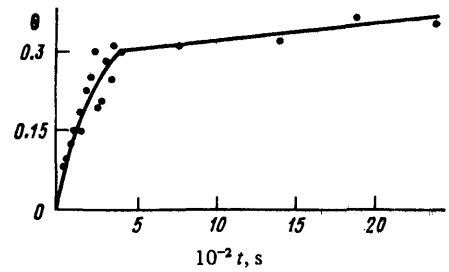


Figure 7. Dependence of the degree of surface coverage θ of iron on the exposure time t in H_2O vapour.

The data in Fig.7 show that, in the adsorption of the dissociation products of water molecules, $\theta = 0.3$ is attained fairly rapidly after which the rate of surface coverage decreases significantly and that, for an exposure of iron to water vapour $>10^4$ *L*, no growth of the oxide film is observed[30]. The low values of θ for which a significant inhibition of adsorption is attained demonstrate, in our view, a strong interaction of the adsorbed species on the surface.

Numerous studies have been made of the oxidation of nickel (and particularly of the adsorption of oxygen and other oxidants) by electron spectroscopy. In the first of these[34] the X-ray electron spectra of nickel were obtained before and after its treatment with oxygen and water vapour. It was also shown that the oxide film on nickel consists of NiO. Other workers arrived at the same conclusion[35]. The surface of nickel has been investigated[36,37] by XES for very low exposures in oxygen (exposure <2 *L*).[37] For such small exposures, a bulk-phase oxide film was not formed on the surface and the chemisorption of oxygen on the nickel surface was investigated.

The X-ray electron spectra of the nickel surface with chemisorbed oxygen served as the basis for a quantum-mechanical model of the formation of the Ni_3O cluster, put forward by Batra and Pobaux[37]. The model of the NiO_6^{10-} cluster has been calculated[38] on the basis of data obtained in the study of the interaction of the (111) face of nickel with oxygen by ultraviolet electronic spectroscopy and low energy electron diffraction.

The results of a detailed investigation of the oxidation of Ni single crystals [(111), (110), and (100) faces] and polycrystalline nickel in the range 30–70 °C with the aid of UPES and XES have been described[39]. It was observed that the initial stage of the interaction with oxygen constitutes dissociative chemisorption for all four types of surface. For a coverage equivalent to ~0.2 of a monolayer, the chemisorption structure comprises adsorbed oxygen atoms distributed on the surface of the nickel support. With increase in the degree of surface coverage to 0.8 of a monolayer, the oxygen atoms are arranged at the lattice sites between the surface nickel atoms. With increase of exposure, the oxygen atoms penetrate into the bulk of the nickel specimen and form a three-dimensional oxide with an average thickness of ~18 Å. This oxide layer is a non-stoichiometric nickel oxide NiO.

The oxidation of nickel was investigated also by the authors of the present review[40]. The results are fully correlated with the conclusion[39] that the oxidation of nickel proceeds via a chemisorption stage. Furthermore, it has been shown[40] that the chemisorbed oxygen on the surface of nickel exists together with the three-dimensional oxide. This is indicated by the data in Fig.8.[40] The figure shows that the X-ray electron spectra of the O 1s line, corresponding to oxygen on the surface of nickel (at 20 °C), undergo a significant change not only in intensity but also in form with increase of exposure. If, after etching with Ar^+ ions the surface gives rise to a low-intensity peak with a maximum at 531 eV (curve *1*) corresponding to a small amount of oxygen, then exposure to oxygen, equal to 20 *L* (curve *2*), does not increase significantly the intensity of the peak, but causes its appreciable broadening. Fourier analysis of this structure yields two peaks with $E_b = 529.5$ and 531 eV. An increase of exposure (curves *3* and *4*) leads to an increase of the intensity of the O 1*s* peak and to a change of the intensity ratio of the two peak components. According to some investigators[35,39], E_b for electrons corresponding to the O 1*s* line of NiO is 529.5 eV. On the other hand, according to Joyner and Robertson[41], the presence of adsorbed oxygen increases E_b by 1.5 eV, which yields 531 eV in our case.

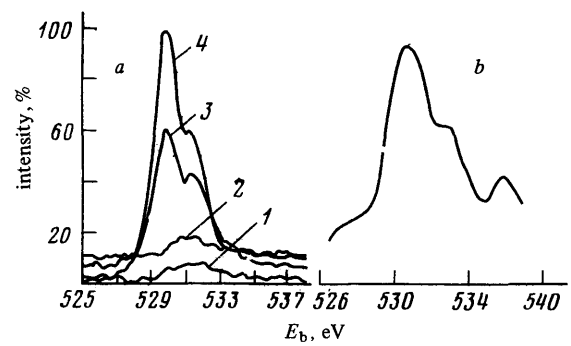


Figure 8. *a*) X-Ray electron spectra of the O 1*s* line on exposure of nickel to O_2 at 20 °C [exposure (in Langmuirs): 1) 0; 2) 2; 3) 10^3; 4) 10^5]; *b*) X-ray electron spectra of the O 1s line on heating an oxidised nickel surface in a vacuum of $\sim 10^{-10}$ mmHg at 100 °C.

Thus the change in the structure of the O 1*s* peak on interaction of nickel with oxygen indicates the existence of only adsorbed oxygen on the nickel surface in the initial stage of the interaction and the existence of oxygen in two states—adsorbed and "oxide"†—in subsequent stages of the oxidation. Heating of the oxidised nickel *in vacuo* ($\sim 10^{-10}$ mmHg) to 100 °C diminishes somewhat the oxide component and the O 1*s* doublet is better resolved (Fig.8*b*).

The oxidation of aluminium was investigated by AES and layer-by-layer etching of the oxide by a beam of Ar^+ ions in a study[42] which is largely of methodological importance. A study[43] of the kinetics of the adsorption and oxidation of aluminium, magnesium, and manganese, and chromium is of considerable interest, the oxidation of aluminium and magnesium having been investigated in greatest detail. The

†A state analogous to that of oxygen in the nickel oxide NiO.

information obtained[43] is of extreme interest also because the interactions of metals with oxygen and water vapour were studied simultaneously by two methods: XES and the method of piezoquartz weighing. The quartz resonator was mounted directly in the preliminary treatment chamber of the electron spectrometer. Data were obtained[43] for both the chemical composition of the surfaces of the oxides and for the dependence of the adhesion coefficient of the oxidant molecules on the exposure and hence on the chemical composition of the surface. The experimental demonstration of the direct proportionality between the change in the intensity of the peak of the O 1s line and the amount of adsorbed oxygen on the above metals must be regarded as an important result of the investigation[43]. The possibility of the formation of both the oxide MgO and the hydroxide $Mg(OH)_2$ on the surface of magnesium when it interacts with water vapour was demonstrated[43]. ΔE_b for these compounds amounted under these conditions to 2.5 eV according to the data of the above investigation. The oxidation of magnesium has been studied in greater detail by Akimov et al.[44], who obtained the electron spectra of the O 1s line, confirming the conclusion[43] that a mixed oxide, consisting of magnesium oxide and hydroxide, is formed on the magnesium surface on interaction with water vapour (Fig.9). This is indicated both by the values of E_b corresponding to the O 1s doublet and by the ΔE_b for these peaks. With increase of the exposure of the magnesium surface in water vapour, the relative amount of $Mg(OH)_2$ also increases. The ratio of the amount of magnesium hydroxide to that of the oxide is stabilised for an exposure of 20–30 *L* and amounts to 0.45; the overall thickness of the oxide film is then also stabilised.

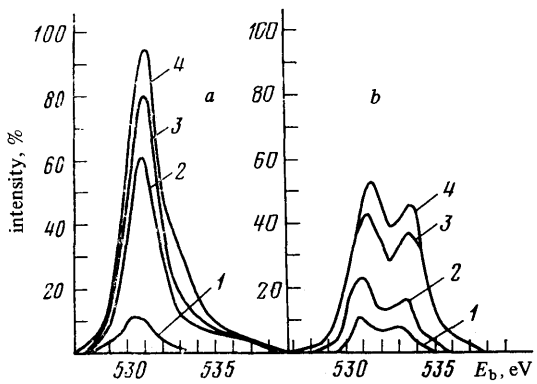


Figure 9. X-Ray electron spectra of the O 1s line on exposure of magnesium to O_2 (*a*) and to H_2O vapour (*b*); exposure (in Langmuirs): *a*: 1) 0.75; 2) 8; 3) 25; 4) 3100; *b*: 1) 5; 2) 10; 3) 25; 4) 10^4.

The oxidation of titanium has been studied by XES.[45–48] An investigation[45] of the electrons corresponding to the Ti $2p_{3/2}$ line for an oxidised titanium surface and titanium oxides showed that the ΔE_b for the Ti $2p_{3/2}$ electrons in TiO and TiO_2 amount to 1.9 and 5.4 eV respectively (relative to the same line for titanium in the zero oxidation state). These data differ from the values of ΔE_b for TiO and TiO_2 published previously[46] (1.0 and 4.9 eV). However, the results of Grant et al.[47] and additional data[48], also published by Simon et al.[45], demonstrate the validity of the values obtained by the latter workers[45]. The value of the study by Simon et al.[48] also lies in the fact that these workers elucidated the composition of the surface in the oxidation of titanium as a function of temperature at an oxygen pressure of ~10^{-5} mmHg. Furthermore, Simon et al.[48] established the values of ΔE_b for titanium compounds such as the carbide, nitride, and hydride, which are respectively 1.8 ± 0.2, 2.2 ± 0.2, and 0.6 ± 0.2 eV.

A study of the oxidation of alloys showed that certain effects can be observed only with the aid of electron spectroscopic methods. Thus a study[49] of the composition of the surface of Au–Ni alloys showed that, when oxygen was adsorbed, the concentration of gold on the surface increased by a factor of 100 compared with the bulk phase and, conversely, the adsorption of hydrogen caused an enrichment of the surface in nickel. The enrichment of the surface in indium on Au–In alloys has been observed with the aid of AES.[50]

The enrichment of the surface in tin following the oxidation of an Ag–Sn alloy has been observed[51] by XES, its extent increasing on heating the alloy. A study of the oxidation of Ni–Al alloys[52] containing between 10 and 30% of nickel, in air at temperatures in the range 20–450 °C showed that aluminium predominates on the surface and determines the behaviour of the alloy on oxidation, even after treatment with alkali, which tends to remove aluminium from the surface. A significant change in the composition of the surface of the alloy has been observed in a study[53] where the oxidation of platinum–rhodium alloys was investigated in air at temperatures up to 1000 °C with the aid of XES and the mass spectrometry of secondary ions. The authors[53] found a significant enrichment of the surface in rhodium at alloy oxidation temperatures close to 1000 °C.

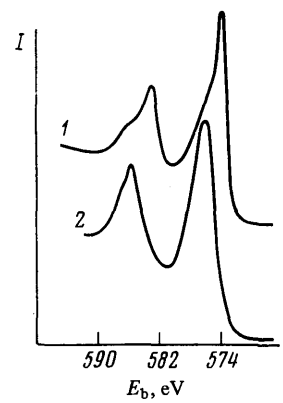


Figure 10. X-Ray electron spectra of the Cr 2p line obtained on oxidation of massive chromium (curve *1*) and the 86% Fe + 14% Cr alloy (curve *2*).

The dependence of the surface concentration of chromium in the $Fe_{0.84}Cr_{0.16}$ single crystal on the oxygen pressure has been investigated[54]. The authors concluded that the change in the ratio of the concentrations of chromium and iron on the surface is associated with the difference between the free surface energies and oxygen affinities of chromium and iron. The oxidation of Fe–Cr alloys in oxygen and water vapour has also been studied by Akimov et al.[55] at ~300 K and oxygen and water vapour pressures in the range 10^{-7}–10^{-5} mmHg.

They investigated the kinetics of the oxidation of these alloys and determined the compositions of the oxide films formed on their surfaces. It was found that the oxide films consist of a mixture of Fe_3O_4 and Cr_2O_3. Comparison of the X-ray electron spectra (Fig.10) of the Cr 2*p* line for the oxidised surface of chromium (curve *1*) and the oxidised surface of an alloy of 86% of iron and 14% of chromium (curve *2*) shows that chromium in the massive state and in the alloy is not oxidised in the same way. Indeed, the chromium in the massive state is oxidised at low oxygen pressures to give a stable oxide film with a thickness equivalent to 2–3 monolayers[10], which is manifested by a slight "bulge" on the Cr $2p_{3/2}$ peak on the high-energy side. The chromium in the alloy with iron is wholly oxidised to Cr_2O_3 for the same exposures, which follows from the shift of the E_b for the Cr $2p_{3/2}$ peak (curve *2*). This difference in the oxidation of chromium in the alloy and in the massive state can be accounted for by the absence of kinetic control in the oxidation of chromium in the alloy, which shows in its turn the absence of aggregates made up of chromium atoms from the oxide film, i.e. the oxide film consists of a solid solution of Cr_2O_3 in Fe_3O_4.

V. ELECTROCHEMICAL PROCESSES AND METAL CORROSION

The electrochemical reactions occurring at the metal–electrolyte interface can lead to a significant change of the chemical composition of the surface of the metallic electrode. These changes are very often localised in a thin surface layer ~100 Å thick. In this case a quantitative analysis of the changes in the chemical composition of the electrode surface can be performed only by electron spectroscopic methods. Here one should recall that such analysis cannot be performed *in situ* and in each specific case one must therefore estimate the possibility of undetectable changes in the chemical composition of the surface associated with the removal of the electrode from the electrochemical cell.

One of the first studies of the application of XES in the investigation of the changes in the chemical composition of the metal as a result of chemical and electrochemical reactions in a metal–electrolyte system was one[56] where the composition of the surface of the platinum electrode was determined (indicated in weight percentages in the Table below) in the course of its treatment in concentrated nitric acid and electrochemical oxidation in 1 *N* $HClO_4$.

The composition of the platinum electrode surface.

Surface compound	HNO_3	Potential in 1.0 *N* $HClO_4$		
		0.7 V	1.2 V	2.2 V
Pt	41	56	39	34
PtO (ads.)	39	39	37	24
PtO	14	5	24	22
PtO_2	6	0	0	20

The tabulated data could not be obtained by any other method and, although the absolute values obtained in the above study[56] give rise to doubts[57], the value of this investigation consists primarily in the fact that the scope of XES in the study of the metal–electrolyte interface was demonstrated.

The electrochemical oxidation of platinum and gold in sulphuric acid has been studied[57] with the aid of XES. It was shown that the oxide layers on platinum begin to be formed at potentials in the range 0.6–0.7 V# (in the same solution); PtO_2 appears at potentials of 1.2–1.3 V. The oxide film on gold consists of Au_2O_3. The thickness of the oxide layers and the true electrode surface areas have been estimated[57]. An important result is the observation[57] of the reduction of platinum and gold oxide under the influence of X-rays; this fact, which was disregarded by Kim et al.[56], can have a significant effect on the results of X-ray electron spectroscopic studies.

The modifications of a tin oxide surface of the electrode formed on adsorption of aminopropylethoxysilane $(C_2H_5O)Si.(CH_2)_3NH_2$ on the latter have been investigated[58] with the aid of XES. It was shown that the adsorption of this substance leads to the formation of covalent –Sn–O–Si– bonds on the electrode surface. The results of the analysis of the X-ray electron spectra are in good agreement with those obtained in the measurement of the impedance in the electrode–electrolyte system.

The surface films arising on a gold electrode in the electrochemical reduction of the Cr^{6+} ion have been studied in an investigation[59] where the gold electrode was polarised in 1 M chromic acid mixture and a mixture of 1 M chromic acid and 0.01 M sulphuric acid. The dependence of the chemical composition of the surface on that of the solution and the electrode potential has been investigated[59] by XES; furthermore, the changes in the thickness of the surface layer, formed on gold following the adsorption of various complexes arising as a consequence of the electrochemical reduction of Cr^{6+} ions, have been studied by analysing X-ray electron spectra.

The chemical composition of the surface of an iron electrode ("Armco") has been investigated[60] by XES in a neutral solution to which a series of oxo-anions, used as corrosion inhibitors, were added. The following salts were studied: Na_2WO_4, Na_2MoO_4, Na_3VO_4, $NaVO_3$, and Na_2CrO_4. The salt concentrations in the electrolyte corresponded to the protective concentrations found as a result of separate experiments. The results[60] permit the following conclusions.

1. All the oxo-anions investigated are strongly chemisorbed on the iron surface, behaving at the same time as acceptors, which follows from the somewhat higher values of E_b for the Fe $2p_{3/2}$ electrons compared with E_b for the Fe $2p_{3/2}$ electrons in the case of Fe_2O_3.
2. On chemisorption, the oxidation state of all the oxo-anions, except the chromate anions, remain unchanged.
3. The entire chemisorbed chromate is reduced, undergoing a transition from the +6 oxidation state to the +3 oxidation state.
4. On chemisorption of the oxo-anions (with the exception of chromate), the oxide Fe_2O_3, in which part of the oxygen has been substituted by the oxo-anions, is present on the surface.
5. The anomalously high protective capacity of chromate compared with other oxo-anions can apparently be accounted for by the existence of a stable complex, the formation of which is probably associated with the reduction of the CrO_4^{2-} anion on the surface of iron.

The study of the interaction of organic inhibitors with the surfaces of metals and alloys is of considerable interest. The interaction of metal ions with the inhibitor results in the formation of complexes whose solubility is fairly low and which are deposited on the surface of the metal. These complexes can in fact enter into the composition of the protective surface layer, which prevents the oxidation of the metal.

#Here and henceforth the potential is given relative to the normal hydrogen electrode.

Despite certain difficulties, particularly the necessity to remove the specimen from the working solution and to transfer it through the atmosphere (although the latter can be eliminated by employing a preliminary chamber filled with nitrogen or another inert gas), promising data have been recently obtained with the aid of XES.[61,62]

For example, surface layers formed as a result of the interaction of benzotriazole with copper (benzotriazole inhibits the corrosion of copper in chloride solutions) have been studied[61]. It has been shown that the protective film consists mainly of the copper(I) complex of benzotriazole. These data were compared with the results obtained with the aid of infrared reflection spectroscopy and the authors[61] were able to estimate the thickness of the surface film as a function of the method of treatment of the specimen.

In the study of the interaction of the surface of iron with organic molecules containing amino- and cyano-groups, it was shown that the interaction of iron with the amino-group results in a considerable decrease in the positive charge on the iron atom and an increase of the positive charge on the nitrogen atom as a result of the formation of the Fe ← N coordinate bond.

However, one should note that there have been as yet no studies of the interaction of the metal surfaces with inhibitors. Furthermore, studies of the interaction of metal surfaces with volatile inhibitors, in which one could carry out experiments in the spectrometer chamber without contact of the specimen with the atmosphere, are apparently of interest.

The interest in the problem of the passivity of metals led to a number of investigations involving the study by electron spectroscopic methods of passive oxide films on the surfaces of metals, in the first place iron and its alloys. The passive films on an iron electrode in neutral borate solutions have been studied[63,64]. Auger spectra have been obtained[63] with layer-by-layer etching of the passivating oxide film on iron with Ar^+ ions, which was formed in the anodic oxidation of an iron electrode in a borate buffer (pH 8.4); its thickness did not exceed 50 Å according to the authors[63], who concluded that a two-layer model is suitable for the oxide film on the iron surface, the inner and outer layers consisting of Fe_3O_4 and γ-Fe_2O_3 respectively.

Different oxide phases, formed on iron under different oxidation conditions, have been studied[64] by AES. The authors[64] were able to distinguish different oxide phases on iron: FeO, Fe_3O_4, Fe_2O_3, and FeOOH. However, the conclusions reached in the above studies[63,64] can hardly be regarded as unambiguous. Apart from the disadvantages of the AES in quantitative analysis described above, this is also indicated[65] by studies of the degradation of the passivating film on iron when the specimen is heated *in vacuo*[65]. According to Revie et al.[65] heating of the specimen leads to irreversible changes in the oxide film associated with the decomposition of OH^- ions. The exposure of the oxide film to a beam of primary electrons, used to generate Auger electrons, can lead to analogous results.

The X-ray electron spectra of chrome and chrome-nickel steels in $1N\ H_2SO_4$ have been obtained[66] and interpreted over a wide range of potentials. It was shown that, depending on the electrode potential, the surface can be enriched in iron or chromium, i.e. the possibility of the selective dissolution of chrome steels was confirmed. It was observed[66] that the surface of steel electrodes exposed at a potential of −0.4 V (the potential corresponding to the maximum rate of anodic dissolution of chromium) is significantly enriched in iron; the opposite behaviour is observed when the electrodes are maintained at −0.15 V. At this electrode potential, which corresponds to the maximum rate of the anodic dissolution of iron, the surface is enriched in chromium. The enrichment of the surface in nickel was not observed.

The influence of silicon on the electrochemical behaviour of Ni–Si alloys (silicon concentration from 0.1 to 3.3 wt.%) in $2N\ H_2SO_4$ has been studied[67]. The silicon concentration on the surface was determined by XES. It was shown[67] that the introduction of silicon into the alloy increases the repassivation currents by two orders of magnitude. Chemical analysis of the surface showed that this effect is associated with a change in the surface concentration of silicon when the electrode potential is altered. It was found that the silicon is present on the surface in two oxidation states (+2 and +4).

The states of the surface of a nickel electrode in the active and passive regions have been studied by different methods[68], including XES (the electrolyte was $1N\ H_2SO_4$). The X-ray electron spectra obtained confirmed that, at potentials more positive than 0.6 V, films of the nickel oxide Ni_2O_3 are formed on the nickel surface. The formation of this oxide terminates at potentials of ~1.0 V. At potentials more negative than 0.6 V (but corresponding to the passive region) an NiO film is present on the nickel surface.

The dependence of the composition (atomic ratio of magnesium and aluminium) of the surface of aluminium bronze in seawater on the electrode potential has been studied by XES.[69] The relation obtained is satisfactorily consistent with the electrochemical idea that the layer near the electrode becomes more alkaline in the cathodic range of potentials and more acid in the anodic range.

The joint application of the technique involving the etching of the surface with a beam of Ar^+ ion and the XES method permitted a layer-by-layer analysis of the passive films formed on chrome steels[70,71]. The surface layer formed on binary Fe–Cr alloys $\{40 \leq [Cr] \leq 30$ wt.%$\}$ following the exposure of the specimens to doubly distilled water freed from oxygen has been investigated at 25° and 70 °C.[70] It was shown that in all cases the concentration of chromium in the surface layer of the oxide increases near the oxide–medium interface; the concentration of chromium on the surface varies linearly with its volume concentration, but dc_S/dc_V increases with temperature (c_S and c_V are the surface and volume concentrations of chromium in the alloy). The passive layer consists of a two-layer film, in which the outer layer consists of chromium hydroxide $Cr(OH)_3$, while the mixed oxide $Fe_{1+x}Cr_{2-x}O_4$ is located closer to the metal. A model of the interaction of steel with water has been proposed[68].

The influence of the same medium and temperatures as in the study of Olefjord and Fischmeister[70] on a chrome-nickel steel (18/8 steel) has been investigated[63]. Castle and Clayton[71] were able to achieve a milder etching of the surface by Ar^+ ions and to obtain a larger number of points on the concentration profiles, which makes their result more reliable. The thickness of the oxide films was 15–30 Å. The composition of the surface oxide includes Cr^{3+}, Fe^{2+}, and Fe^{3+} bound to OH^- or O^{2-} ions. The authors[71] believe that the selective oxidation or dissolution of the components of the steels is ruled out.

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The above examples of the application of the XES, AES, and UPES methods in the study of the interaction of the surfaces of metals and alloys with the external medium show that, with their aid, it is possible to obtain very valuable and sometimes unique information about the nature of the chemical interactions occurring on the surfaces and in the surface layers of solids. Application of electron spectroscopic methods in combination with mass-spectrometric and diffraction methods yields a fully quantitative picture of the complex chemical processes occurring on the surfaces of metals when the latter interact with various media and makes it possible

to identify reliably the chemical transformations already in the chemisorption stage when the degree of surface coverage is much less than a monolayer.

Naturally, the analytical possibilities of the above methods are not of interest solely to specialists working in the field of oxidation, corrosion, and electrochemistry, although the examples of the application of the methods refer to these particular fields. One should note that a number of reports containing extensive data on the application of XES, AES, and UPES in the study of adsorption and catalytic processes have now been published[72-75]; furthermore, a collection of reports[76], published in Russian translation in 1979, is extremely useful to investigators becoming acquainted with the applications of electron spectroscopic methods.

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Internal Reflection Spectra of Surface Compounds and Adsorbed Molecules

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The application of attenuated total reflection (ATR) spectroscopy in surface studies of inorganic adsorbents and catalysts, polymers, and optically transparent electrodes is discussed. The basic principles of ATR spectroscopy as applied to surface phenomena are considered, with special reference to thin films, industrial adsorbents and catalysts, and polymer degradation processes. 276 References.

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I. INTRODUCTION

Since the first report (Fahrenfort, 1961) of spectral measurements on a condensed phase by attenuated total internal reflection[1] the ATR (attenuated total reflection) method has been widely used in practical spectrochemical studies[2-5].

The basic principles of attentuated total reflection spectroscopy and of its applications have already been discussed in monographs[5,6] and reviews[7-13]. The rapid development of practical applications was helped by the discovery of high refractive index materials transparent in the infra-red, by new mathematical methods of describing the ATR spectra, and by the appearance of special attachments for all types of i.r. spectrometer, allowing single (ATR) and multiple (MATR) internal reflection. The wide appeal of the method is explained also by the similarity between the ATR and the transmission spectra, both in the position of the bands and in the validity of Beer's law.

However, in spite of the outward similarity between ATR and transmission spectra, there is a fundamental difference, associated with the form of the electromagnetic field interacting with the sample. When the spectrum is recorded under ATR conditions the electric vector of the light wave near the interface between the sample and the prism retains all its three components, and as a result the ATR spectra (unlike the transmission spectra) give information on the dipoles oriented at right angles to the surface. Hence, the surface and the bulk properties of solids can be studied simultaneously by the combined use of ATR and transmission spectra.

A large amount of experimental information on surface phenomena obtained by the ATR method is now available. New variants of internal reflection spectroscopy include spectrorefractometry, Raman spectroscopy, liquid ATR spectroscopy, studies of chemical reactions and of adsorption on flat surfaces, and the use of optically transparent electrodes in electrochemistry. New develoments in methods of obtaining the ATR spectra of surfaces and in the study of surface compounds and of adsorption on sorbents, catalysts, polymer surfaces, and electrodes are reviewed in this paper.

II. BASIC PRINCIPLES OF THE ATTENUATED INTERNAL REFLECTION SPECTROSCOPY METHOD

The ATR spectra are produced by the high sensitivity of the reflection coefficient R to changes in the absorption coefficient κ and, to a smaller extent, in the refractive index n. By optimising the experimental conditions we can minimise the sensitivity of the spectra to changes in n while retaining their sensitivity to changes in κ. This is achieved by suitable choice of the angle of incidence: a few degrees greater than the critical angle ($\sin\theta_{crit} = n_2/n_1$, where n_2 is the refractive index of the unknown material and n_1 is the refractive index of the ATR attachment, with $n_1 > n_2$). The spectra recorded with $\theta > \theta_{crit}$ show very little distortion of the bands, though the intensity of the bands is greatly reduced. Stronger bands can be obtained by increasing the number of reflections: the method is then called the MATR (multiple attenuated total reflection) method. The spectra measured with $\theta \cong \theta_{crit}$ can differ very substantially from the absorption spectra, but they offer a high contrast even after a single reflection. The choice of the method of producing the spectrum (ATR or MATR) depends on the specific features of the problem.

1. Principles of Quantitative Analysis by ATR Spectroscopy

Quantiative analysis by ATR spectroscopy consists in determining the optical constants n and κ from the ATR spectra of the experimental materials by using the Fresnel formulae. The spectra obtained from multi-layer systems, or substances having a surface layer of variable concentration, can be analysed by using the generalised Fresnel formulae sometimes called the recursion formulae[14,15]. Since the calculation can be carried out on a computer the use of the recursion formulae offers a flexible method of quantitative analysis in ATR spectroscoy, because most surface concentration profiles can be modelled as multi-layer systems on a computer. Various approximations are used in analytical practice to describe the dependence of the reflectance coefficient R on the absorption (or on the concentration) by means

of simple expressions. These approximations are obtained by expanding the R coefficient in a power series of the adsorption coefficient κ.[16] The expression proposed by Harrick[5] is the simplest and the most widely used.

The reflectance coefficient R under conditions of internal reflection can be expressed as

$$R = 1 - \alpha d_{\text{eff}},$$

where $\alpha = 4\pi\kappa\nu$ is the absorption coefficient, and d_{eff} is the effective thickness. At low absorptions ($\alpha d_{\text{eff}} < 0.1$) this expression is equivalent to approximating R by a series expansion in α truncated after the first term. Hence, since the attenuation of the light intensity after a single reflection is small, the experimetnally measured reflectance coefficient can be expressed as

$$R = e^{-\alpha d_{\text{eff}}}.$$

For large samples, of thickness much greater than the wavelength of the light ($2\pi d/\lambda_1 > 1$), we have the following expressions for parallel and for perpendicular polarisation of the incident light respectively:

$$\frac{d^{\perp}_{\text{eff}}}{\lambda_1} = \frac{n_{21}\cos\theta}{\pi(1-n_{21}^2)\cdot(\sin^2\theta - n_{21}^2)^{1/2}} \qquad \frac{d^{\parallel}_{\text{eff}}}{\lambda_1} = d^{\perp}_{\text{eff}} \cdot \frac{2\sin^2\theta - n_{21}^2}{(1-n_{21}^2)\sin^2\theta - n_{21}^2},$$

where $n_{21} = n_2/n_1$ is the relative refractive index. In both cases the effective thickness decreases as θ increases, and increases with the wave length of the light in the optically denser medium ($\lambda_1 = \lambda/n_1$).

Several authors have used the Beer–Lambert law in spectro-analytical ATR work. Calibration curves (optical density against concentration) were used to analyse polyester layers[17,18], for the quantitative determination of vinyl acetate in the polyethylene copolymer[19] used as a surface-active additive to Nylon-6,[20] to monitor the extent of reaction during the synthesis of epoxy resins[21], and for the quantitative determination of carbonyl compounds in polyethylene[22].

In the case of a thin film on a transparent substrate (n_3), and assuming that the conditions $2\pi d/\lambda_1 < 0.1$ and $\kappa < 0.1$ apply, the effective thicknesses can be obtained to a good approximation from the expressions

$$d^{\perp}_{\text{eff}} = \frac{4n_{31}d\cos\theta}{1-n_{31}^2}, \qquad d^{\parallel}_{\text{eff}} = d^{\perp}_{\text{eff}} \frac{(1+n_{32}^4)\sin^2\theta - n_{31}^2}{(1+n_{31}^2)\sin^2\theta - n_{31}^2}.$$

By comparing the expressions for thick samples and for thin films we note that the ATR spectra of thin films are similar in many ways to ordinary transmission spectra. Thus, their intensity is independent of the wave length, and in the neighbourhood of the critical angle the changes in d_{eff} are gradual. In thin films $d^{\perp}_{\text{eff}}$ can be greater than or smaller than $d^{\parallel}_{\text{eff}}$, depending on the relative values of n_1 and n_2, and both these parameters can be substantially greater than the geometric thickness of the sample.

The spectral changes in the absorption coefficient α can be found by measuring R. The integral characteristics of the bands also are calculated from the ATR spectra, using the more convenient Γ-integral (related to the usual A-integral ($A = \int \alpha d\nu$) by the simple expression $\Gamma = A\nu_{\max}$)[23]. Since $\alpha = Kc$, where K is the molecular absorption coefficient and c is the concentration, we have

$$R = e^{-Kcd'_{\text{eff}}/\nu},$$

where $d'_{\text{eff}} = d_{\text{eff}}\nu \cdot n_1$. Therefore we can write

$$\Gamma = \int \alpha \frac{1}{\nu} d\nu = \frac{1}{cd'_{\text{eff}}} \int \ln\frac{1}{R} d\nu.$$

If the Γ-integral is expressed in the dimensions of cm^2 mole^{-1} the intensity of the fundamental vibrations lies in the range 10^2–10^5, and that of the overtones in the range 1–100.

In practice the Kramers–Kronig method[24] is used most often to evaluate n and κ, because it requires only half as many measurements as the two-angle method[5]. The Kramers–Kronig calculations rely on reference values ("tie-values") of n and κ, known for one or two points in the integration region:

$$\varphi(\nu_0) = -\frac{\nu_0}{\pi}\int_{\nu_{\text{init}}}^{\nu_{\text{fin}}} \frac{\ln R(\nu)}{\nu^2 - \nu_0^2} + C_1(\nu_0) + C_2(\nu_0),$$

where ν and ν_0 are the time-dependent and the fixed wave number, ν_{init} and ν_{fin} are the limits of the integration range, and C_1 and C_2 are correction terms[24]. Having calculated $\phi(\nu_0)$ we can find the "amplitude" reflection coefficient

$$\hat{r}(\nu_0) = R^{1/2} e^{i\varphi(\nu_0)},$$

which is related to n and κ (for perpendicular polarisation) by the expression

$$\hat{r}_{\perp} = \frac{(\bar{n}_2^2 - n_1^2\sin^2\theta)^{1/2} - n_1\cos\theta}{(\bar{n}_2^2 - n_1^2\sin^2\theta)^{1/2} + n_1\cos\theta},$$

where $\bar{n}_2$ is the complex refractive index of the material ($\bar{n}_2 = n_2 - i\kappa_2$). The first attempt to measure n_2 and κ_2 from ATR infrared spectra by this method[11] gave satisfactory results.

Some regions of the spectrum of fused quartz[25] are shown in Fig.1 to illustrate the comparison of bulk and surface properties in terms of measurements of optical constants by different methods. The absorption by the surface layers of SiO_2, given by the ATR measurements, is quite different from the bulk optical properties of quartz. The results shown in Fig.1 are qualitatively consistent with measurements on a quartz sample in optical contact with a Ge ATR cell, and with measurements by the liquid technique[68].

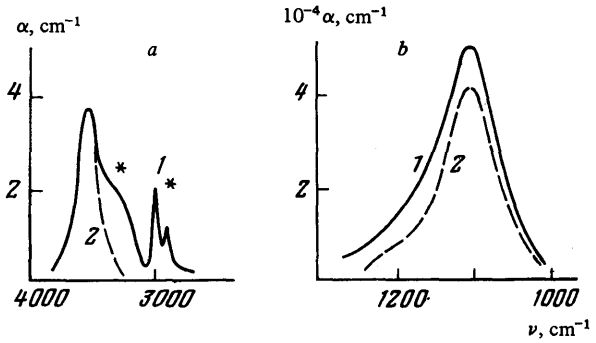


Figure 1. Optical properties of polished fused quartz, measured by different methods: (*a*) *1*) ATR method, *2*) transmission method; (*b*) *1*) ATR method, *2*) external reflection method. The asterisks denote bands due to adsorbed water and hydrocarbons.

Direct quantiative studies of substances supported on solid surfaces are complicated by the need for an ideal contact between the sample and the ATR cell (which is readily achieved in the case of liquid samples). Some workers assume that a "physical contact" is adequate for measurements of n

and κ, others make a correction for the transition layer (or gap) by using an intermediate value of the refractive index[26–28]. In some cases "optical contact" between the surfaces is successfully established, giving reliable measurements on strong bands, but is is claimed[29] that a gap of 40–100 Å is still present, though it does not substantially affect the measurements if the material which fills the gap by capillary condensation (usually water) is transparent in the chosen spectra region. In the case of measurements in the absorption band of the adsorbate (i.e. in the transmission region of the substrate material) even such a small gap can produce unexpected results, since the topography of the surface will produce a gap at the contact between the two solid surfaces, and as a result of capillary forces this gap will contain a thin layer of water and hydrocarbons. These effects are more marked when the surfaces are etched.

The possibility (in principle) of obtaining accurate values of n and κ from a solid surface can be realised in practice by using liquid ATR spectroscopy in the visible[5] or the i.r. region[30]. This variant has been used to study pentacene films adsorbed on crystalline or glassy substrates, and also the surface properties of poly(tetrafluoroethylene) (Teflon-4) in thin-film and in massive samples[30]. Immersion liquids having a specially high refractive index have proved very useful in this work.

An important practical contribution to this type of measurement was a detailed study[31] of the dependence of the results on the quality of the optical contact and on the size of the air gap beween the polymer sample and the MATR cell, with a description of an attachment for pressing the sample controllably against the cell. An apparatus including such an attachment is described also in Ref.32.

Modified variants of ATR spectroscopy have been used in recent years (in addition to the more traditional ATR methods) to study solid surfaces[33–35]. In all these variants a gap, usually air-filled, is present between the sample and the ATR cell when a spectrum is recorded from a flat surface. Under these conditions the incident light interacts with surface vibrations (polaritons) which are non-radiative, i.e. they are not detected under normal conditions such as in transmission spectra. Studies of the spectroscopic characteristics of polaritons give information on the dynamics of the crystal lattice. Experiments of this type, with alkali halide crystals, were first reported in Ref.36. The method was used also to study the surface of a series of uniaxial crystals[37], including α-quartz[38,39].

In studies of finely divided media by the ATR method surface polariton bands can appear in the spectrum close to strong bands from the crystalline powder[40]. The intensity and shape of the latter will be largely determined by the crystal habit of the particles and by the polarisation of the incident light. It has been shown[40,41] that whereas external reflectance spectra consist mainly of bands from transverse vibrations of the crystal lattice the ATR spectra tend to reveal longitudinal and surface vibrations. It should be noted that the study of adsorption on powders not previously treated (e.g. by pressing) requires a large number of reflections (50–100), as well as an expanded photometric scale.

In work with relatively coarse particles distortion of the bands (or even the appearance of new bands) is possible, and model calculations of the reflectance spectra must be carried out to avoid incorrect interpretation of the experimental results. Thus, a simple multi-layer model has been used[41] to calculate the ATR spectra of powders and fibres from the Fresnel formulae for multi-layer systems[14]. The effective reflectance coefficient R of such a system for a plane wave can be expressed as a statistical sum in the case of cylindrical fibres. It is assumed that the optical properties of each layer are equivalent to those of one fibre. If the diameter of the fibre is $d \gg \lambda$, and $\theta \gg \theta_{crit}$, the integration can be replaced by a summation with $\theta = \text{const}$.[44]

A convincing test of this model, made with fused quartz fibres 10 and 50 μm in diameter, gave excellent agreement between calculation and experiment, especially with perpendicular polarisation[42]. The advantage of using a model approach is clearly demonstrated in Refs.42 and 43, where a system of new, very strong i.r. bands at 1100–900 cm^{-1} (which are not found in transmission) is satisfactorily interpreted by using a somewhat more detailed model of close-packed quartz fibres 10 μm in diameter (see Fig.2). In the case of spherical particles the R coefficient must be calculated with allowance for the increase in the relative contribution to R with the number of steps when the sphere is divided into flat layers. These problems are highly relevant to the future application of MATR spectroscopy in studies of industrial adsorbents and catalysts, most of which are used in a powder or fibre form, and also in studies of polymer fibres.

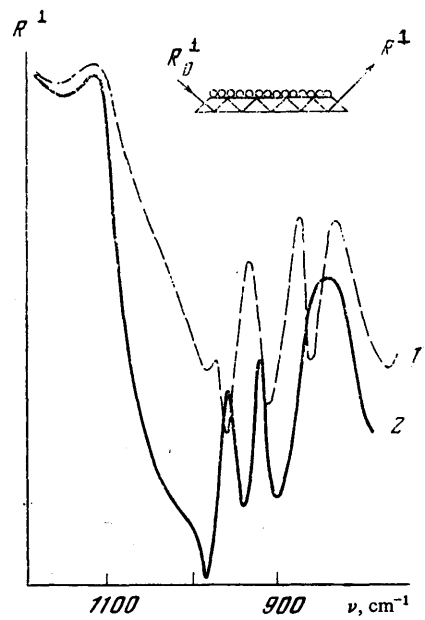


Figure 2. Comparison of experimental (*1*) and calculated (*2*) MATR spectra for close-packed quartz fibres 10 μm in diameter[43].

The roughness of surfaces with a fine finish has been studied[44] by using a model of the surface consisting of a system of intermediate layers with gradually varying values of n and κ. SiO_2 and LiF crystals were studied in the "residual ray" region. The optical properties of the transition

layer were modelled by the Lorentz–Lorenz equation in the complex form

$$\frac{\bar{n}_l^2-1}{\bar{n}_l^2+2}=\frac{\bar{n}_M^2-1}{\bar{n}_M^2+2}V+\frac{\bar{n}_s^2-1}{\bar{n}_s^2+2}(1-V),$$

where $\bar{n}_l$, $\bar{n}_s$, and $\bar{n}_M$ are the complex refractive indices of the layer of roughened surface, of the substance filling the uneven regions of the surface, and of the material M at a given depth within the sample respectively, and V is the proportion by volume of the bulk phase in the layer M. This approach has proved very successful in quantitative studies of the state of water and hydrocarbons adsorbed on micro-heterogeneous polished surfaces[29,45,46], and also in the study of microporous films[44,47–51].

2. Thin Films

Quantitative studies of thin films offer entirely new possibilities in the application of spectroscopic methods to practical problems in micro-electronics, integrated optics, and laser technology. However, allowance must be made for possible non-uniformities in very thin films, especially discontinuities in properties over the thickness of the film and roughness of the substrate surface, both of which can influence the optical properties of the film. The molecular adsorption of water on a polished fused quartz surface has been studied extensively[52–55], and the optical properties of the water film on an undulating surface with a small-scale roughness of 40–100 Å were shown to be markedly dependent on the optical characteristics of the substrate material and on the type of micro-roughness.

By allowing for these factors in the use of the Lorentz–Lorenz equation we conclude that the intrinsic spectroscopic properties of water in layers more than 10 Å thick (i.e. the shape and intensity of the stretching and bending vibration bands) are similar to those for ordinary liquid water. On the other hand, direct measurements of the refractive index of water in the very thin (~12 Å) gap between two flat surfaces in "optical contact" have revealed a clear dependence on the refractive indices of the two surfaces in contact.

A method of calculating the primary and the secondary structure of a polished surface has been developed from these these observations[45]. When the surfaces are brought in contact at a relative humidity of 50–60%, corresponding to an average thickness of 12 Å for the adsorbed water layer, the bending vibration at 1620 cm^{-1} shows a strong anomaly: its intensity is about 4 times greater than that of the corresponding band for liquid water[52]. As the relative humidity is increased the layer becomes thicker, and its optical properties become indistinguishable from those of liquid water at a thickness of 40 Å, but if the water layer is subsequently thinned the shape of the spectrum is unchanged (i.e. the spectrum does not revert to its initial state). Many hydrocarbon contaminants have been detected on these surfaces. The removal of these contaminants, which appear to be a residue from surface etching treatments, combined with special treatments to give hydrophilic surfaces, should enable thicker layers of water to be sorbed on the surface by a multimolecular mechanism. Comparison with ellipsometric measurements can be valuable, because very accurate thickness measurements on very thin films are possible by ellipsometry. The measurements suggest that the specific absorption of light by surface defects exceeds bulk absorption almost 100-fold[56].

Ellipsometry has been effectively combined with ATR spectroscopy in studies of the transition layer at the semiconductor–dielectric interface[57]. The adsorption of CO_2 on Si,[58] of H_2O on α-quartz[58], of proteins on polymers[59], and of proteins on carbon[60] have also been studied. As well as flat interfaces, layers adsorbed by porous systems have been examined by the ATR method[48–50,61].

3. Apparatus

A wide range of ATR and MATR attachments, mainly for the i.r. region, is now avaiable commercially. Apparatus for measurements in vacuum and at different temperatures is being developed[62,63], including the special MNPVO-3 MATR attachment which can be used with Soviet spectrophotometers (IKS-14, -22, -16, -29) as well as with the UR-20. This apparatus has already been used in a number of investigations, and has yielded very interesting results[29,43,45,52]. A vacuum adsorption cell is described also in Ref.64.

Attempts to develop a liquid-phase version of ATR spectroscopy resulted in the production of various attachments for the visible region[65]. Liquid MATR cells have been based on liquid chalcogenide glasses, especially As_xBr_yS, which are transparent in the i.r. region.[66–69] The standard ultra-high refractive index immersion liquids (with refractive indices up to $n = 2.1$) were shown[52] to have a set of wide transmission "windows" at 4000–750 cm^{-1}, making them suitable for use in ATR spectroscopy. Media with $n \geq 2.4$ have also been discovered.

Instrumental developments in ATR spectroscopy include, in addition to the construction of new attachments for the spectrophotometer, new designs of high-precision apparatus. These include the IRF-461 spectrophotorefractometer, developed for the simultaneous and accurate determination of both the optical constants n and κ of the complex refractive index[70]. Another recent development is the ISN-1, a multi-purpose industrial MATR spectrophotometer[71,72] which can be applied to a wide range of surface investigations.

The high sensitivity of the combination of MATR with Fourier spectrometers has allowed, for example, the measurement of MATR spectra in the i.r. region on polybutadiene filled with Aerosil and carbon black (up to 20 parts by weight per 100 parts of elastomer). The technique is particularly useful in studies of optically transparent electrodes, which attenuate the light beam up to 100-fold. Various problems in electrochemistry have been solved by using MATR cells coated with a film (up to 800 Å thick) of gold, platinum, or other conductor.

Plasma techniques have been used to clean the surface of ATR cells. Practical recommendations on the alignment of the apparatus and on corrections for a number of systematic errors (convergence of the light beam, uncertainty in the number of reflections, error in the angle of incidence) are made in Ref.11. Some of the recommended assemblies[11] have been used by other workers to determine n and κ for a number of liquids[73–79].

III. ADSORPTION

1. Surface Chemistry

The surface compounds which determine the selectivity of adsorbents and the catalytic properties of catalysts have been studied intensively by i.r. spectroscopy[80,81]. Whereas the transmission variant of i.r. spectroscopy is usually adequate for finely divided adsorbents and catalysts, having a large surface area, the MATR method has to be used to study the surface chemistry and the adsorption phenomena

of thin films supported on massive solids (silicon or germanium crystals, quartz, various glasses, crystals of halide salts, etc.)[82-84]. Special vacuum cells have been developed for MATR studies of surface compounds and adsorbed molecules[64,85].

The influence of surface treatment on the optical properties of the constituents of MATR cells has been studied in several laboratories. Surface treatment of a silicon MATR prism by hydrogen ions produces an absorption band at 2062 cm^{-1}, assigned to vibrations of the Si–H groups[86]. When silicon MATR elements are heated in water absorption bands due to amorphous silica appear at 1600–1850 cm^{-1}.[87] The MATR spectrum of thermally oxidised silicon includes absorption bands at 1870 and 1620 cm^{-1} (Si–O vibrations)[81]. Absorption bands from the OH group (3630–3650 cm^{-1}) and from the Si–H group (2250 cm^{-1}) are found in the spectrum of a silicon sample bombarded with phosphorus ions and heat treated in hydrogen[88]. Anodic oxidation of a silicon surface produces absorption bands from hydrogen-bonded hydroxyl groups in the MATR spectrum. Free hydroxyl and hydride groups have have been observed[89] on a silica surface heated at 1050° to 1200 °C in oxygen and water vapour. Molecular deposition reactions, in which the surface of a Si or Ge prism is treated with $SiCl_4$ or $GeCl_4$, produce strong bands at 1070 cm^{-1} (SiO_2) or 860 cm^{-1} (GeO_2, hexagonal) in the MATR spectrum[90-92].

MATR studies of porous silica films up to 1000 Å thick have yielded valuable information on the surface chemistry of this system. The films were prepared on the surface of MATR plates, and used as models of highly disperse adsorbates based on silica. One method of deposition used in this work was by electron-beam evaporation of crystalline silicon[47]. The initial spectrum of a film deposited on quartz by this method[85] included a broad absorption band at 3000–3700 cm^{-1}. Heating the sample to 50 °C produces bands at 3640 and 3460 cm^{-1}. When the temperature is raised to 150–200 °C the band at 3460 cm^{-1} is almost completely suppressed, and a band appears at 3670 cm^{-1}. After treating the sample in vacuum at 350–400 °C a band is observed at 3700 cm^{-1}, but the band at 3670 cm^{-1} does not disappear fully even after baking at 450 °C.[85]

Similar changes in the MATR spectrum have been reported for silica films deposited on silicon prisms[93] by the hydrolysis of $SiCl_4$ vapour at room temperature or from alcoholic solutions of $Si(OC_2H_5)_4$. Molecular water was found[93] to be almost completely removed by pumping at 35 °C. After dehydroxylation at 200 °C the spectrum shows an absorption band from hydrogen-bonded surface hydroxyl groups (at 3520 cm^{-1}) and a band from free hydroxyl groups on the micropore surfaces (at 3680 cm^{-1}). Only the absorption band for the free groups (at 3700 cm^{-1}) remains after vacuum treatment at 400 °C. The shift of this band by 50 cm^{-1} as compared with the free hydroxyl group band on Aerosil (3750 cm^{-1}) [81] is explained by perturbations of these groups through interactions with the oxygen atoms of the micropores.

A systematic study of hydrolysis reactions on the surface of quartz glass, and of their relevance to surface defects in glass and hence to the strength of glass, has been undertaken by the MATR method[94-100]. An absorption band at 3650 cm^{-1} and a weaker band at 3500–3550 cm^{-1} can be observed in the MATR spectrum of the surface layer of quartz glass. The absorption band due to adsorbed water molecules disappears after the prism is heated to 300 °C.[95] The influence of the thickness of the layer containing hydroxyl groups, and of the polarisation state of the light, on the precision with which the concentration of hydroxyl groups in quartz glass can be determined by the MATR method has been the object of a special study[96].

The hydrolysis of a quartz glass surface in a saturated aqueous solution of silica at 200–300 °C is discussed in Ref.97. The real strength of the glass (with surface defects) was found to increase with the temperature and the duration of the immersion in the aqueous solution. This effect is ascribed to preferential hydrolysis of the most highly stressed siloxane bonds on the surface of the glass. The strength of etched quartz glass has been shown to depend on the hydrolysis of a small proportion of the surface bonds[98]. The hydrolysis of quartz glass in an autoclave at 70–240 °C affects a surface layer 2–10 μm thick[99]. On the other hand, the nucleation and fast growth of all types of defect, accompanied by a large decrease in strength, occurs at the cristobalite (200–300 °C) and quartz (570–600 °C) phase transition temperatures of the crystalline modifications of silica[100].

The surface chemistry of other solids also has been studied. Thus, the MATR spectra of polished samples of gallium arsenide which had been stored in water show absorption bands at 700 cm^{-1} (Ga–O, As–O), 1550 cm^{-1} (Ga=O, As=O), and 850 cm^{-1} (Ga–OH, As–OH).[101]

MATR studies of the surface chemistry of powdered adsorbents deposited on a prism have been less successful, owing to the limited volume of material which can be irradiated. The MATR method has been used[102] to study the spectrum of surface hydroxyl groups in powdered α-quartz of 0.5 μm particle size. After heat treatment in vacuum at 200 °C the powder gave narrow symmetrical bands at 3649 and 3627 cm^{-1}, which were assigned to two different types of free hydroxyl group on the surface. The absorption bands from structural hydroxyl groups in zeolite (at 3740 cm^{-1}) were shown[103] to be much weaker in the MATR spectra than in transmission spectra.

The MATR method is very valuable in surface studies of carbon adsorbents, which end to absorb and scatter the i.r. radiation[104-107]. Thus, MATR spectroscopy has been used[104] to identify the functional groups on active carbon surfaces. The MATR spectra (at 1000–2000 cm^{-1}) of sugar charcoal activated in O_2 or $CO_2 + O_2$ atmospheres denote the presence of surface carbonyl and carboxyl groups[106]. Carbon films deposited in a vacuum on a KRS-5 element were investigated[107]: after being oxidised in a solution of $K_2S_2O_8$ these films gave absorption bands from CO groups (at 1710 and 1736 cm^{-1}) and bands from aliphatic CH groups (at 2850 and 2920 cm^{-1}).

The spectrum of a Cu film 20 Å thick deposited in a vacuum on a KRS-5 prism and subsequently exposed to the air showed absorption in the region of 700–320 cm^{-1}, consistent with the formation of Cu_2O.[107]

2. Adsorbed Molecules

MATR has been used as a very sensitive method of checking the freedom from organic contaminants of single-crystal silicon surfaces. The sensitivity of the detection of aliphatic organic compounds on the surface of a silicon element is 3×10^{-9} g cm^{-2}, and higher than the sensitivity of the methods of surface control used in the electronic components industry[108]. When the element has been washed in de-ionised water the MATR spectrum is found[109] to include absorption bands from the stretching vibrations of CH groups in aliphatic hydrocarbons present on the surface at a concentration of 3×10^{-8} g cm^{-2}. Heating the silicon plate in alcohol causes partial removal of the surface oxide layer, together with its associated organic contaminants[110,111].

The adsorption of stearic acid molecules on single-crystal surfaces has been studied in detail[112–116]. Sharke[112] examined the monolayers of stearic acid and its esters on germanium prism. The sensitivity of the detection, using the absorption bands of C–H and C=O stretching vibrations, was 2.3×10^{-7} g cm^{-2}. Dimeric molecules of the fatty acid are adsorbed preferentially from solutions of stearic acid in CCl_4 of 0.005–0.01% concentration[113]. The interaction between stearic acid molecules and a silicon surface is reported[113] to be significant only at solution concentrations >0.01%, though the effects become noticeable even at lower concentrations if the adsorbed water molecules are previously removed.

The MATR method[114] has been used to measure the adsorption isotherm of stearic acid from CCl_4 solution on the surface of a silicon prism (curve *2* of Fig.3). The result is compared with the Gibbs adsorption isotherm in curve *1* of Fig.3. The concentrations of adsorbed molecules were determined after removing the prism from the solution. The sensitivity of the detection of stearic acid on the prism from the 2920 cm^{-1} band was 3×10^{-9} g cm^{-2}. The portion of the isotherm near the first point of inflection (at low concentrations) corresponds to the surface area occupied by one molecule of stearic acid (154 Å), and is consistent with a planar orientation of the molecules along the prism surface. The region of almost constant surface concentrations, in equilibrium with concentrations of $2–3 \times 10^{-4}$ mole fraction, corresponds to a sloping portion of the Gibbs adsorption isotherm, for which the surface is covered with a monolayer of molecules oriented at an angle to the surface. The point of inflection (curve *1* of Fig.3) at an equilibrium concentration of 4×10^{-4} mole fraction corresponds to an area of 20.5 Å^2 per molecule, and therefore indicates molecular orientation at right angles to the surface in the close-packed monolayer. The MATR spectra of adsorbed stearic acid molecules measured at the points of inflection of the isotherm are consistent with a change in orientation of the molecules, from planar through sloping to vertical. These changes are accompanied by an increased contribution from the "crystalline" form of the adsorbed molecules.

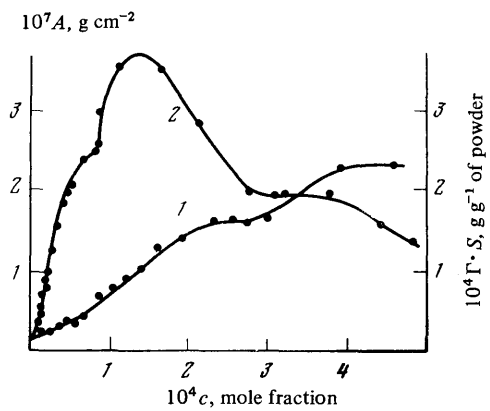


Figure 3. Adsorption isotherms for stearic acid on silicon: *1*) Gibbs adsorption (Γ) on powdered silicon from CCl_4 solutions; *2*) surface concentration of stearic acid (A) adsorbed on a silicon MATR prism from solution in CCl_4 (S is the surface area of the powder)[114].

Polarised MATR spectra give additional information on the orientation of adsorbed molecules. Takeneka and coworkers[116] studied the polarised MATR spectra of molecular layers of stearic acid deposited on the surface of a germanium prism by the Langmuir–Blodgett method. They concluded that these films consist of a system of monoclinic crystals, oriented with their C axis at an angle varying from 217° to 35° (depending on the number of layers) to the normal to the stearic acid–germanium interface. Preferential growth of these crystals takes place in the plane parallel to the stearic acid–germanium interface. The thickness of a monolayer is 23.8 Å.

The aggregation and the orientation of large flat molecules on the surface of MATR elements has been studied also by other workers[117,118].

The spectrum of a monolayer of ethyl octadecanoate molecules on the surface of a germanium prism includes an absorption band for free CO groups (1745 cm^{-1}), but not for hydrogen-bonded CO groups (1710 cm^{-1}).[103] This shows that hydrogen bonds are not formed between molecules in the adsorbed state. Reaction between the carbonyl groups and the Ge surface is observed after lengthy storage.

The polarised MATR spectra in the visible region for Methylene Blue adsorbed on a glass prism surface are discussed in Ref.117. Adsorption cuases a change in the relative intensity of the absorption from monomeric (600 nm) and dimeric (660 nm) molecules, as well as the appearance of a new absorption band at 740 nm. These spectral changes are ascribed to preferential adsorption of the dimeric form. The polarisation measurements indicate a parallel orientation of the adsorbed molecules.

Polarised MATR spectra have been used[118] to study the orientation of 1,1-diethyl-2,2-carbocyanine bromide molecules on silver chloride and glass surfaces. On a silver chloride surface these molecules are adsorbed as aggregates or micelles, in which the plane of the molecules is perpendicular to the surface. On the other hand, on a glass surface the adsorption is mainly molecular, or in small aggregates of the sandwich type. Under the latter conditions there is no preferential orientation of the molecules with respect to the surface.

Very interesting results have been obtained from MATR studies of adsorption on adsorbents and catalysts of industrial importance, and on models of these adsorbents. The state of the adsorbate has been characterised by MATR studies of these materials in the form of oxide films on the surface of the optical elements. The small thickness of the films (<1 μm) and, therefore, the low absorption and almost total lack of scattering of the i.r. radiation ensure that the adsorbate is detected with a high sensitivity[119]. The sensitivity of detection of adsorbed water by the MATR method (using the 1625 cm^{-1} band) is 0.03% of a monolayer[93].

The adsorption properties of films prepared on the surface of silicon elements by the hydrolysis of $SiCl_4$ vapour are determined by the microporous structure of the film[93]. These films can adsorb water molecules, but not ethanol molecules: in other words, their pore diameter is $<4.7 \times 10^{-4}$ μm. Silica films prepared from alcoholic solutions of $Si(OC_2H_5)_4$ have a looser structure.

The adsorption of water molecules by films which have been dehydroxylated at 400 °C causes hydroxylation of the micropore surface[93]. The absorption bands produced by the adsorption of water molecules correspond to bending vibrations of the dimeric molecules (at 1625 cm^{-1}) and to stretching vibrations of the OH group in the strong hydrogen bond region (3300 cm^{-1}, see Fig.4). This suggests the formation of two types of hydrogen bond by the adsorbed molecules: with the oxygen atoms of the surface hydroxyl groups and

with the oxygen atoms on the micropore surfaces. Heating the films in air (to 400 °C) does not lower the adsorption of water molecules, but sintering effects are produced by heating the porous films to 700 °C.[120]

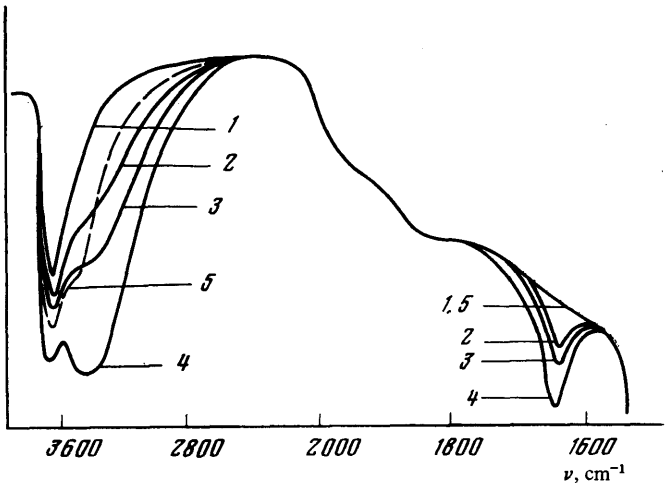


Figure 4. Infrared MATR spectra of water adsorbed on a silica film baked in vacuum at 400°: *1*) initial film, stored in vacuum at 30°, *2*) after adsorption of H_2O at 0.33 mmHg, 3) ditto at 0.8 mmHg, 4) after 4 days in contact with H_2O vapour at 0.8 mmHg, 5) after freezing out the H_2O vapour with liquid nitrogen[93].

The methods of quantitative evaluation of the MATR spectra (see II, 1) allow us to determine the amount of water adsorbed and to calculate the volume and diameter of pores in the film[47,62]. Absorption bands at 3650 and 3550 cm^{-1} were observed[47] in the MATR spectrum of SiO_2 films prepared by electron-beam evaporation in a vacuum and allowed to adsorb water from a moist atmosphere. The water content was determined from the intensity of the 3550 cm^{-1} band in films of different thickness prepared in different ways, and the pore volume was calculated in each case. An average pore diameter of 5–7 Å was obtained[47].

Changes in the MATR spectrum produced by the adsorption of $CHCl_3$ on films of this type heated to different temperatures indicate sintering effects at temperatures as low as 100 °C.[85]

MATR spectroscopy has been used[121] to determine the water content of thin films of SiO_2, MgF_2, and ZnS deposited by vacuum evaporation on Si, Ge, and KRS-5 prisms. The layers were shown to be fully saturated with water after admission of air at a relative humidity of 60–70% into the vacuum chamber. The changes in optical characteristics of the layer are throught to be due to the increased refractive index produced by the filling of the micropores by water molecules.

ZnS films prepared by laser evaporation in air have also been examined[51]. Their MATR spectra contained bands due to adsorbed water and hydrocarbon molecules.

The pore surfaces of films prepared by vacuum evaporation may contain, in addition to hydroxyl groups, other adsorption centres of the acceptor type which can induce major changes in the electronic structure of adsorbed molecules. Thus, anomalous band intensities as well as new absorption bands are observed[119] in the MATR spectra of $CHCl_3$ and CCl_4 molecules adsorbed on Ge and MgF_2 films evaporated in a vacuum by the electron beam method. Most of the water adsorbed on gallium arsenide layers was found[101] to be in a molecular form, attached to the surface by donor–acceptor bonds.

The MATR spectra of all the films obtained by vacuum deposition of SiO_2, ZrO_2, GeO_2, In_2O_3, Al_2O_3, NdO, MgF_2, SrF_2, NdF_2, CaF_2, ZnS, and Sb_2S_3 were found to contain an absorption band due to adsorbed water (3350 cm^{-1}). Various studies of the effect of deposition rate, residual gas pressure, and substrate temperature on the porosity of these films have been reported[62,122,123].

The MATR spectra of molecules adsorbed on single crystals of aluminium oxide are particularly interesting, because this compound is widely used as an adsorbent and a catalyst. The polarised MATR spectra of surface hydroxyl groups have been measured[124] on the (0001), (1123), and (4150) faces of an α-Al_2O_3 crystal. Molecular orientation in monolayers of calcium stearate and n-pentanol on the (4150) face was determined, and the adsorption isotherms were measured on all three faces at 30–120 °C. The isosteric heats of adsorption for a film 0.4 of a monolayer thick on the (0001), (1123), and (4150) faces were 13, 19, and 26 kcal $mole^{-1}$ respectively.

The MATR spectra of stearic acid molecules adsorbed from CCl_4 solutions on Ge and on Al_2O_3 (0001 face) prisms have been studied[115] with a Fourier spectrometer. The maximum detection sensitivity was 0.03 of a monolayer. The authors discuss in detail[115] the application of MATR spectroscopy to adsorption and desorption kinetics, adsorption isotherms, adsorbent–adsorbate interactions, molecular orientation, and to the structure and chemisorption of layers of adsorbed molecules.

The polarised spectra of CO molecules adsorbed on palladium salts deposited on the surface of a NaCl prism have been measured[125]. The low-frequency absorption bands (<1800 cm^{-1}) are assigned to CO molecules adsorbed with a high heat of adsorption (~40 kcal $mole^{-1}$) on Pd atoms from low-index crystallite faces, whereas the absorption bands at 1800–2000 cm^{-1} are associated with bridging structures found only on some of the faces of the Pd crystallites. Linear surface structures are found on Pd atoms of all the faces of the crystallites.

MATR spectra have been used[106,107,117] to study adsorption on opaque carbon films. The spectra of *p*-nitrophenol adsorbed on charcoal[106] and on carbon black[117] are consistent with the formation of donor–acceptor complexes with surface carbonyl groups. The spectra of albumin adsorbed on evapported carbon films have also been described[107].

The MATR method is also being applied to studies of biological materials, including bacteria[126]. A method of measuring the adsorption and desorption isotherms of water on protein films deposited from aqueous solutions on the surface of a KRS-5 prism has been described[127]. The MATR adsorption isotherms for water molecules on egg albumen and on tropomyosin were shown to be identical to those given by the MacBain balance.

The MATR method can be used also to study molecules on powdered adsorbents. Thus, it has been applied in the identification of compounds in chromatographic spots in the

separation of mixtures of *o*- and *p*-nitrotoluenes with 2,4-dinitrotoluene and of a mixture of *o*-, *m*-, and *p*-anisidine[128], and in the separation of steroids by thin-layer chromatography[129]. The MATR spectra of the dye Crystal Violet adsorbed on silica gel[130] and of ethyl xanthogenate on the surface of copper powder particles[131] have also been reported.

We should stress the need for the utmost caution in interpreting the spectra of adsorbed molecules near strong absorption bands due to the adsorbent[132], because bands from surface polaritons can appear in the MATR spectra of powders on the high-frequency wing of the adsorbent band (see II, 1).

IV. PHYSICAL CHEMISTRY OF POLYMER SURFACES

ATR spectroscopy has been applied very effectively to studies of polymeric materials, whose physical and mechanical properties are very well adapted to the technique. The possibilities of the method in studies of the surface layers of polymers have been demonstrated in several investigations[133–141].

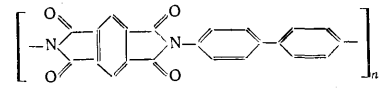
A series of papers[142–144] deals with the molecular mechanism of polymer degradation under mechanism load, and explains the role of surface layers in the degradation of polymers. The concentration of defects produced by the breakdown of macromolecules has been determined in low-pressure, intermediate-pressure, and high-pressure polyethylene (PE),[144] in rubbers and vulcanised products from natural and synthetic latex[142,143,145], and in poly(ethylene terephthalate) (PETP).[146] When the samples are subjected to mechanical load the concentration of end-groups in a surface layer 1 μm thick becomes 1–3 orders of magnitude greater than in the bulk (depending on conditions). Macroscopic cracks in the surface layer become saturated with decomposition products of the polymer molecules[143]. Using the shift of the vibration frequencies in the i.r. spectrum produced by mechanical loads, the stress in loaded PETP samples was shown to be as high as 700 kg mm^{-2}, i.e. close to the theoretical strength of the material[146]. The overloaded bonds are the first to break under the influence of thermal fluctuations, and therefore the enhanced concentration of these bonds in the surface layer (one order higher than in the bulk) explains the important role played by the surface layer in controlling the degradation of polymers under mechanical stress.

In ATR spectroscopy the absorption depends on the direction in which the radiation is polarised[5]. With anisotropic samples, the advantages of ATR measurements in polarised light over ordinary absorption spectroscopy include the possibility of studying strongly absorbing materials, the decoupling of the absorption coefficients for the three spatial directions (k_x, k_y, k_z),[147] and the possibility of studying the orientation of molecules on the surface independently of their orientation in the bulk.

Flournoy developed the theory of the interaction of a damped light wave under ATR conditions with an anisotropic medium[147], and he subsequently used it[148] to determine the orientation of macromolecules in uniaxially oriented films of polypropylene. Among the many investigations using polarised light one of the most noteworthy is a study[149–151] of the spontaneous orientation in planes of polypeptide and protein macromolecules in the α-form. Planar orientation was shown to occur mainly in a thin surface layer directly adjacent to the substrate, and to become gradually less pronounced with increasing distance from the substrate.

A study[52,153–156] of various polyimides has established the planar orientation of the macromolecules, brought about by cooperative effects involving the macromolecules in media bounded by a planar substrate. The techniques used in the analysis of ATR spectra of fibres (of organic or inorganic origin) are discussed in depth in Refs. 43 and 52. Polarised ATR spectroscopy and wide-angle X-ray diffraction have been used to show that the functional NH and C=O groups in aromatic polyamide fibres are oriented at right angles to the fibre drawing axis[157]. Shushkov and coworkers[158,159] studied the orientation of molecules in polyester fibres, and showed that under axial stretching PETP fibres undergo a transition from folded *gauche* conformations to stretched *trans* conformations. Oriented PETP fibres are discussed also in Refs. 160–162.

The angles between the moments for the vibrational transitions and the axis of the macromolecule have been calculated for several bands in the ATR i.r. spectra[52,154,155,162]. Satisfactory consistency between the spectroscopic results and X-ray diffraction data has been obtained by using the crystallinity bands. Oriented films of polytetrafluoroethylene have been studied by the MATR method using polarised light[163]. The more marked dichroism of the bands at 1150 and 553 cm^{-1} in the MATR spectra (as compared with the transmission spectra) was interpreted as evidence for a greater degree of orientation of the macromolecules in the surface layer than in the bulk. We have compared[164] the surface and the bulk properties of a polyimide film prepared from the dianhydride of pyromellitic acid and 4,4′-diaminophenylene:



By comparing the transmission and the MATR spectra in polarised light we also concluded that states of the macromolecules not found in the bulk are produced at the surface of samples by heat treatment.

The ATR method has been used to study the interaction between poly(dimethylsiloxane) (SKT) and a filler (Aerosil), and the observed spectral effects were explained by the formation of hydrogen bonds between the hydroxyl groups of Aerosil and the Si–O–Si groups of SKT.[165,166] At the same time the orientation of the macromolecules in a uniaxially stretched regular polymer was examined, and it was found that in *cis*-polybutadiene and polyisoprene the surface orientation of the macromolecules varies with time, the dichroic ratios of some of the bands reaching a maximum several days after mechanical treatment of the sample. The longer relaxation times of the surface layers were ascribed to the involvement of supermolecular structures in the rearrangement, in contrast to the bulk orientation effects which involve only segments of the macromolecules. The reorientation time of the supermolecular structures on the surface can be 10^4–10^5 times greater than the reorientation time of the segments in the bulk of a stretched vulcanisate[167]. The ATR method has been used to analyse artificial leather-cloth made from poly(vinyl chloride), polypropylene film, layered plastics, adhesive tapes, carbon-filled (up to 3% and 20% respectively) rubbers[20] and elastomers[168], cellulose fibres[169], and some thermally stable fibres[170].

An investigation of layers of lipids and proteins adsorbed at the water–air interface has been reported[171–173]. Monolayers and multilayers freshly deposited on a germanium MATR element by the Langmuir–Blodgett method (80 reflections) were found to have i.r. spectra similar to those of the corresponding melts. On the other hand adsorbed layers allowed to stand for 160 h on the MATR surface yield bands which are characteristic of the crystalline state. These conclusions are confirmed by electron micrographs of the layers[172]. In two-layer structures the hydrocarbon chains are oriented normal to the surface of the MATR element.

By varying the experimental conditions under which the ATR spectra are recorded (angle of incidence, relative refractive index n_{21}, state of polarisation of the light) the depth of penetration of the light and the effective sampling thickness can be varied between wide limits, thus extending the range of applications of the method to include diffusion problems. The idea was first formulated by Harrick[5], and realised experimentally by Carlsson and Wiles[174-176]. Photooxidation and treatment in a corona discharge of unstabilised polypropylene (PP) produces characteristic hydroxyl (3400 cm^{-1}) and carbonyl (1715 cm^{-1}) bands in both the transmission and the MATR spectra. Using a set of MATR elements made of germanium and of KRS-5 the authors[174-176] varied the relative depth of penetration d_p/λ from 0.066 to 0.201, and this allowed them to observe a gradual decrease in the relative optical densities D_{1715}/D_{2840} and D_{3400}/D_{2840} with increasing depth. The decrease in concentration of carbonyl and hydroxyl groups in a direction normal to the sample surface is approximately exponential.

Subsequently[177-181] the ATR method was used to study the oxidation of polyolefins by ozone by determining the concentration gradients of carbonyl oxidation products in polyethylene. Using a semi-cylindrical ATR element the effective thickness was varied over a wide range by varying the angle of incidence θ. If the sample contains a concentration gradient of more than one group the method gives the overall trend to a good approximation. Plots of $D_{C=O}/D_{C-H}$ against $d^{\perp}_{eff}$ (where $d^{\perp}_{eff}$ is the effective thickness of the layer for perpendicular polarisation of the light) are shown in Fig.5.

The following expression has been obtained[180,181] for the dependence of the concentration of carbonyl products on $d^{\perp}_{eff}$:

$$c_{C=O} = \frac{D_{C-H}}{\varepsilon_{C=O} d^{\perp}_{eff}} \cdot 10^{a/d^{\perp}_{eff}+b},$$

where D_{C-H} is the optical density of the band used as an internal standard, $\varepsilon_{C=O}$ is the molar absorption coefficient, and a and b are empirical constants. Differentiation of these curves with respect to $d^{\perp}_{eff}$ should give the concentration gradients of oxidised groups in depth. As Fig.5*b* shows, most of the carbonyl products of the oxidation of polyethylene by ozone are concentrated in a surface layer a few micrometres thick.

Quantitative tests of the validity of Fick's law in polymer diffusion are conveniently carried out by this approach. The diffusion coefficients of methanol and acetone in polyisobutylene rubber have been measured[182] by the single ATR method. Two thermal diffusion schemes, shown in Fig.6, were used in this experiment. In the scheme of Fig.6*a* the surface *AA'* of the rubber film is in intimate (adhesion) contact with the surface of the ATR element, and its other surface is in contact with the diffusant. In this case the penetration of the diffusant is monitored from the increase in the

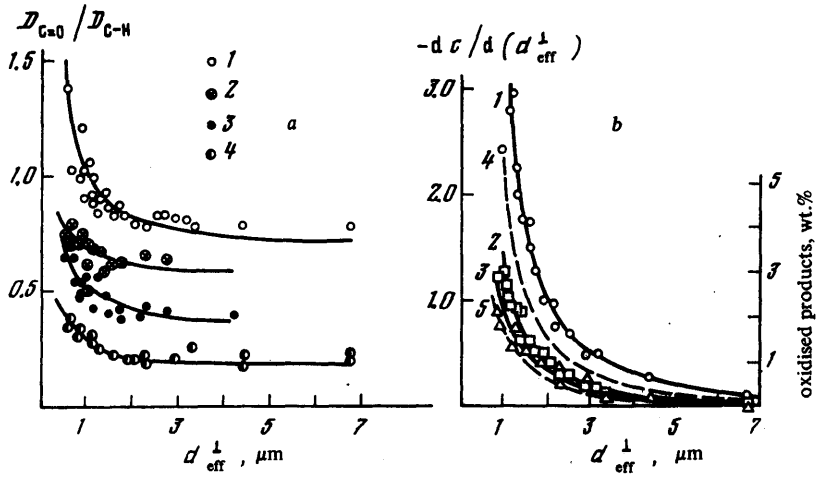


Figure 5. (*a*) Relative optical density $D_{C=O}/D_{C-H}$ against $d^{\perp}_{eff}$ for polyethylene (*1*, *2*) and polypropylene (*3*, *4*) oxidised by ozone: *1*) 170 mg $litre^{-1}$ of ozone, oxidation time 5 h; *2*) 170 mg $litre^{-1}$ of ozone, oxidation time 1 h; *3*) 130 mg $litre^{-1}$ of ozone, 5 h; *4*) 130 mg $litre^{-1}$ of ozone, 1 h. (*b*) plots of $dc/d(d^{\perp}_{eff})$ against $d^{\perp}_{eff}$ for polyethylene oxidised by ozone (170 mg $litre^{-1}$) for different times (*1*) 5, *2*) 1, *3*) 0.5 h), and variation with depth of the concentration of oxidised groups in polyethylene oxidised with ozone (170 mg $litre^{-1}$) for different times (*4*) 5, *5*) 1 h).[181]

relative optical density of the analytical band. In the second scheme (Fig.6*b*) the surface *BB'* (which had been in direct contact with the diffusant) is pressed against the ATR element. The concentration gradients of the diffusant as a function of the film thickness *l* measured in this way are shown in Fig.6*c* for different times t_n. The equation obtained [182] accurately describes the kinetics of the changes in diffusant concentration in the polymer in the direction of d_p and at time *t*.

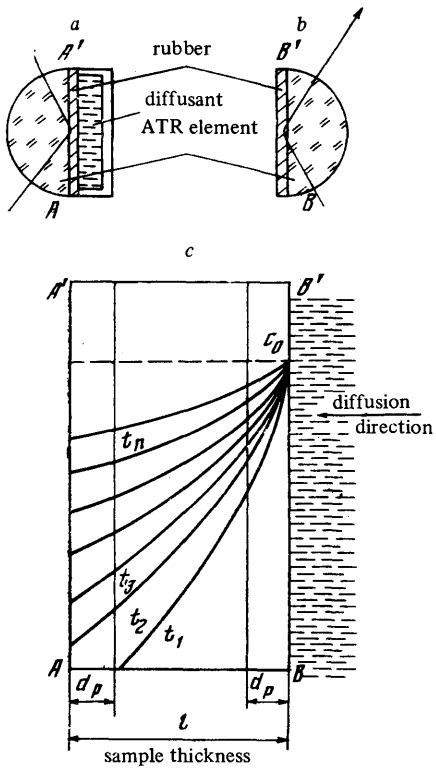


Figure 6. Two arrangements of the diffusion experiment in rubber. (*a*) diffusion monitored from the *AA'* surface; (*b*) diffusion monitored from the *BB'* surface, which had previously been in contact with the diffusant; (*c*) is a schematic presentation of the concentration profile of diffusant through the thickness of the rubber film at different times (t_1, t_2, ... t_n); c_0 is the concentration of diffusant at the surface; the depth of penetration of the radiation is given[182] as $d_p = \lambda_1/2\pi(\sin^2\theta - n_{21}^2)^{1/2}$.

A similar experimental arrangement was used[183,184] to study the diffusion kinetics of non-solvents in elastomers by the MATR method. This approach confirmed[185] the authors' previous suggestion that the surface layer of a polymer in adhesional contact with a solid surface has an abnormally high density. During diffusion, or heat treatment, the macromolecules undergo transitions into more probable conformations, giving a more uniform density distribution.

The diffusion coefficients of ethyl acetate in polyethylene and of ethanol in poly(butyl methacrylate) have been measured[186,187] by applying Fick's equation to the ATR results. By varying the reflection conditions a decrease in the concentration of epoxy resin with increasing distance from the resin–polysiloxane rubber interface was detected[188].

Since the oxidative degradation of polymers often begins at the surface, internal reflection spectroscopy can give important information on the initial steps of the processes involved.

Measurements of the optical density ratio of the bands at 720 and 730 cm^{-1} in the MATR spectra of PE which had been exposed to ozone revealed[189,190] an increase in the degree of crystallinity, arising from the preferential "combustion" of the amorphous phase[191]. By combining ATR measurements with electron microscopy and low-angle light diffraction it was established that in linear polyethylene the supermolecular formations in a surface layer ~1 μm thick are the same as those in the bulk. However, there are large differences in internal structure between the bulk and the surface: the crystallite orientations are different, and the amorphous regions of the surface layer contain an abnormally high proportion of folded molecules with a large number of defects. The main difference between the surface layer and the bulk lies in the structure of the molecules in the amorphous regions[152]. It has also been shown, by the MATR method, that previously unknown but stable hydroxy-, keto-, and alkoxy-acids with a very low content of C–H bonds can be produced by deep oxidation of PE with ozone[189].

The mechanism of the oxidative degradation of PE at the copper–PE interface is discussed in Refs.192 and 193. It is shown that the formation of carbonyl-containing products is markedly accelerated at a surface in contact with copper, and that the MATR spectrum of the copper surface contains bands suggesting the formation of carboxylic acid salts which act as catalysts for the oxidation of the PE.

Accelerated photo-oxidation of PE in the presence of titanium dioxide[194], and the effect of thermal and oxidative degradation on the adhesion of PE to aluminium[195,196], have been reported. The dependence of adhesion on the time of heat treatment goes through two maxima, which are explained by postulating simultaneous oxidation and structural rearrangement processes in the surface layer of PE. Experiments on the adhesion of PE to a quartz MATR element led to the hypothesis that hydrogen bonds can be formed between functional groups on the PE surface and the surface hydroxyl groups of the quartz[197].

Under practical conditions the surfaces of many materials are exposed to corona discharges, and therefore particular attention has been devoted to this type of interaction. For example, polytetrafluoroethylene has been exposed to air and to ammonia under corona discharge conditions[22]. In the air atmosphere volatile degradation products are formed, and desorbed from the PE surface, whereas in the ammonia atmosphere surface modification occurs to a depth of several micrometres. Extensive investigations of the effect of corona discharges on polyolefin surfaces have been reported[174–176]. The infrared ATR spectra of polyamide films which had been exposed to a glow discharge showed intensity changes in the stretching vibration bands of the C–H groups and in the Amide II bands (1550 cm^{-1}), and an increase in the concentration of carbon products[198].

In conclusion we should mention a short review of the application of ATR to studies of polymers and fibres[199], and a useful applied investigation of adhesive tapes in which the effect of the position, size, and shape of the polymer sample on the quality of the MATR i.r. spectra is clearly brought out[200].

V. ELECTROCHEMISTRY

Electrochemists have always been concerned with structural changes on electrode surfaces and in the layer of solution in contact with the electrode, but until recently direct (and non-destructive) methods of observation were not available. Adsorption and reflectance spectrophotometry and ellipsometric methods are now being applied in electrochemistry. A discussion of the whole range of optical methods lies beyond the scope of the present review, and interested readers are referred to recent publications on this topic[201-203]. Some of the most recent work has dealt with an experimental arrangement called the optically transparent electrode (OTE) in the English and American literature, which can be set up by using conventional absorption spectrophotometry[203-205] or ATR spectroscopy[206]. We shall confine our discussion to the OTE relying on internal reflection.

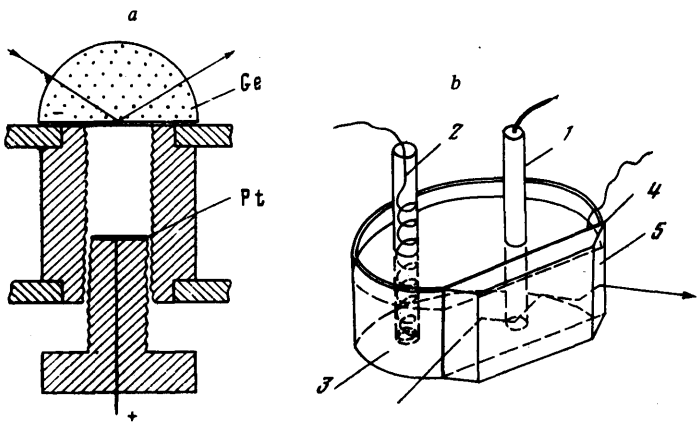


Figure 7. OTE cells based on (*a*) ATR [187] and (*b*) MATR [201] elements: *1*) calomel reference electrode, *2*) external gold electrode, *3*) electrolyte solution, *4*) gold OTE, *5*) glass MATR element.

Ordinary single or multiple reflection elements are used as OTEs in the ATR mode by coating their surface with a thin (200–800 Å) conducting layer of tin oxide, gold, platinum, or carbon. Different types of OTE are described in Ref.12; two examples are shown in Fig.7. These ATR cells are placed in the cell compartment of the spectrophotometer, and the i.r. or u.v. spectra are recorded during the electrochemical experiment. The thin layer of conductor on the surface of the ATR element does not prevent the penetration of light into the electrolyte solution, but it attenuates it very strongly, and therefore the theory of ATR with allowance for thin films and multi-layer coatings must be used in the quantitative evaluation of the results[14,201]. Fig.8 shows the u.v. ATR spectra of a solution of the dye Eosin Y, obtained with an ordinary glass MATR element and with a gold-coated element respectively[201]. The enhanced intensity of the bands in the case of parallel (as opposed to perpendicular) polarisation of the light is consistent with the theory developed by Hansen[16].

The use of MATR elements coated with conducting films introduces complications into the spectral analysis owing to the possibility of resonance effects[207]. Some workers prefer to use uncoated germanium elements (for the i.r. region). Operation in the visible region of the spectrum is thought[201, 206] to offer some advantages: firstly, because electrolytes are usually transparent in this region, and secondly, because effective thicknesses are small and therefore thinner films can be studied, even in the region of light absorption by the electrolyte. The optimum film thickness can be calculated if the optical constants of the medium for the relevant spectral region are known.

In the visible region the depth of penetration of the radiation into the optically less dense medium is ~50 nm. If a compound having a diffusion coefficient of 10^{-5} cm^2 s^{-1} is formed on the OTE surface during the electrochemical process, a concentration gradient falling by 1% at a depth of 400 nm will appear within 1 s. At that depth the amplitude of oscillation of the electric vector of the electromagnetic field is damped to one thousandth of its value at the surface. Thus, rapidly plotted ATR spectra can give valuable information on surface concentration in the case of electrochemical effects on OTEs with time constants of the order of 1 s.

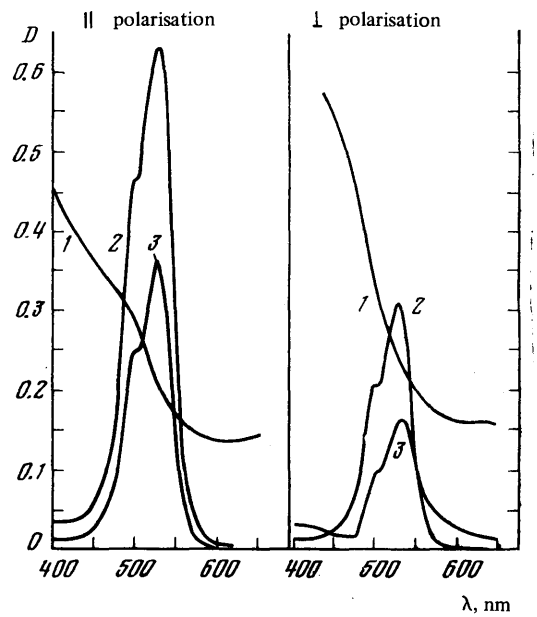
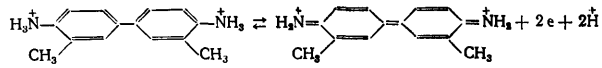


Figure 8. Internal reflection spectra of solutions of the dye Eosin Y: [201] *1*) reflectance spectrum of the gold OTE; *2*) Eosin Y on the gold OTE; *3*) Eosin Y on the glass MATR element.

As an example of this type of problem we may consider one of the earliest OTE investigations[208]: a study of the electrochemical oxidation of *o*-toluidine in hydrochloric acid. A glass plate coated with a film of SnO_2 was used as the MATR

element. The depth of penetratration was ~60 nm. The electrochemical reaction



involved the two-electron oxidation of *o*-dimethyl-*p*-phenylenediamine on the electrode surface with formation of an intermediate product with an absorption band at $\lambda_{max} = 438$ nm. From the time dependence of the optical density D_{438} and of the electrode potential the concentration and the extinction of this compound were calculated, as well as the rate constant of its disproportionation reaction.

An important experimental paper[209] suggests the use of OTEs in quantitative studies of processes as a function of distance from the electrode surface, and considers the electrochemical oxidation of *p*-anisylamine as an example.

OTEs have been used to study a wide range of electrochemical reactions, including the electrochemical behaviour of lithium perchlorate in dimethylsulphoxide on a germanium surface[210], the anodic oxidation of potassium ethyl xanthate in water (by measuring ATR spectra at different values of the anode potential)[211], and the kinetics of the disproportionation of zinc tetraphenylporphyrinate[212]. Among the most important applied investigations is a study[213] of the electrochemical corrosion of germanium in sea water.

Most of the work to which we have referred is aimed at developing applications of the method to specific problems, and it represents a considerable step forward in this direction. However, systematic studies of electrochemical problems exploiting the OTE are far less numerous. One of the best known examples is the work of Trifonov and coworkers, who in 1970 described an ATR apparatus for studying electrochemically induced polymerisation on the surface of a germanium ATR element coated with gold[214]. The apparatus was applied to an investigation of the polymerisation of acrylonitrile induced by electrochemically generated radical anions[214–218]. Most of the measurements were made on the stretching vibration band of the C≡N group. The ATR spectra recorded[215,216] at various stages during the reaction are shown in Fig. 9. Intensity changes of some other bands were also recorded.

As a result of the kinetic study the following scheme was proposed for the cathodic reaction:

$$CH_2{=}CHCN + 2e \rightarrow [CH_2{=}CHCN]^{2-}.$$

Disproportionation of the anion causes the formation of a radical anion:

$$[CH{=}CHCN]^{2-} + CH_2{=}CHCN \rightarrow 2\,[CH{=}CHCN]^{\cdot-}.$$

Recombination of the radical anion produces a di-anion with an extended carbon chain:

$$2\,[CH_2{=}CHCN]^{\cdot-} \rightarrow [CNCH(CH_2)_2CHCN]^{2-}.$$

More recently the method has been used to study the polymerisation of 1-vinylimidazole[219].

Adsorption from solutions is another area of electrochemical research in which ATR techniques are being increasingly applied. Higashigama and Takenaka[220] exposed an electrochemical cell with a germanium electrode to polarised radiation, and they showed that for certain concentrations of sodium laurate in water the adsorbed layer of lauric acid on the OTE surface consists of uniaxially oriented crystallites,

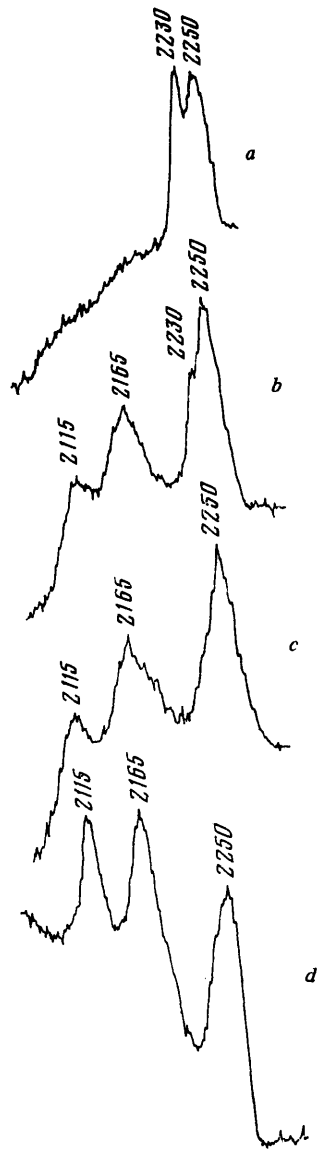


Figure 9. ATR spectra in the stretching vibration region of the C≡N group during electrolysis of acrylonitrile: (*a*) partially polymerised monomer (2230 cm^{-1}, monomer; 2250 cm^{-1}, polymer); (*b*) and (*c*) sequentially recorded spectra showing the appearance of the radical anion (2165 cm^{-1}) and of the radical dianion (2115 cm^{-1}); (*d*) spectrum for the highest achievable concentration of active particles[215].

with their crystal axis inclined at 39° to the normal to the electrode surface. When a critical concentration of sodium laurate is exceeded the adsorption becomes micellar. The effects of potential, pH, and temperature on the adsorption were also studied by the same method.

Two interesting papers[221,222] demonstrate the possibilities of modern infrared techniques. A carbon film 220–300 Å thick was evaporated on a germanium electrode. The transmission of this OTE at 1800 cm^{-1} was only 1.5%, but by using multiple scanning and scale expansion techniques it was possible to study the electrochemical adsorption of fibrinogen on the carbon electrode. The thickness of the adsorbed layer of fibrinogen was shown to be 250–350 Å. Two Amide I bands (1644 and 1614 cm^{-1}) and two Amide II bands (1553 and 1520 cm^{-1}) were observed at a surface potential of +150 mV. It was concluded that after electrochemically induced adsorption the fibrinogen molecules are present in two forms, one of which is stressed and relaxes to the normal form when the potential is removed.

The electrochemical adsorption of Methylene Blue from buffered solutions was studied in the u.v. region[223]; various examples of electrochemical reactions and adsorption on OTE surfaces are discussed in Ref.224.

Optical internal reflection spectroscopy has become one of the basic techniques of research on the physical chemistry of surfaces. The development of experimental techniques has advanced to the point where quantitative measurements can be justified. The topic most urgently in need of further theoretical development is the quantitative analysis of disperse systems by the ATR method.

The procedures so far developed can be used to analyse systems quantitatively in terms of both the optical constants over a wide region of the spectrum. This is important from the standpoint of measurement techniques, and also because it allows new problems to be formulated in surface physical chemistry. Current trends include combining the ATR method with other methods of surface investigation, such as Fourier transform spectroscopy. Internal reflection spectroscopy offers new perspectives in the study of the aggregation and orientation of molecules adsorbed on various surfaces, and important developments can be expected also in this direction.

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Papers published while the present review was in preparation include general discussions of a number of experimental problems in ATR spectroscopy[225–230], and a discussion of a correction for the quality of the contact between the ATR element and the sample[231]. Theoretical models have been used to derive expressions for the concentration gradients in surface layers[232–234], and to compare the surface and the bulk properties of glasses[235], polymer films, and fibres[236–241]. Recently reported studies deal with the influence of surface defects on the strength of polyamide fibres[242], the influence of electrical polarisation on the spectra of polyacrylonitrile[243], and the interactions of ozone with rubber[244] and polypropylene[245] and of a glow discharge with various polymers[246]. The work on the deposition of adsorbed layers of proteins on the surface of MATR elements by the Langmuir–Blodgett method has continued[247–250]. The adsorption of proteins on polyethylene[251], the diffusion of CCl_4 in Teflon[252] and of water in lipid layers[253], processes in photographic gelatin layers[254], and the photo-oxidation of dyes on an optically transparent ZnO electrode[255] have been investigated. New optical media for ATR have been developed[256–259], and industrial spectrophotometers[260–263] and associated equipment[264–267] have been put on the market. The ATR method has been used in Raman spectral studies[268–270], and in various problems in materials science[271], in geochemistry and petroleum chemistry[272–274], and in the protection of the environment[266,275,276].

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Chemical Forms of Mercury, Cadmium, and Zinc in Natural Waters

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Published information on the chemical forms of mercury, cadmium, and zinc in natural wet environments (water, suspended or colloidal particles, deposits, biota) and on their toxicity and biological interconversions is generalised and critically discussed, and the mechanisms for the absorption and expulsion of these materials through the appropriate phase separation surfaces are considered. The chemical forms of these and other trace metals are shown to be the controlling factor in their geochemical cycles and their anthropogenic effects on ecological equilibria in the natural environment. 224 references.

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I. INTRODUCTION

In the natural wet environment metals are found in waters, suspended or colloidal particles, the biota†, and in sludge deposits. Their distribution between these phases is controlled by complex and little understood mechanisms, involving a variety of chemical, physicochemical, biological, and physical processes which can be mutually exclusive or complementary. Existing chemical information and phenomenological models cannot adequately predict the distribution of metals between the various phases in aqueous media, which are usually very complex systems of variable composition. Though the metals are conveyed to the aqueous medium by wind erosion of dry land and by volcanic activity, a significant proportion (at least in some areas) is now contributed by man. Undesirable ecological effects can be expected as soon as the rate of supply of metals to the aqueous medium begins to exceed the rate of supply through the natural cycle: such effects have been noted in inland and coastal waters of industrially developed countries as a result of effluent disposal, of fuel combustion, and of the manufacture of cement. The atmosphere plays an important role in the transport of metals[1].

Large-scale poisoning by mercury and cadmium in Japan[2] dramatically showed that the ability of the natural environment to free itself from chemical substances of anthropogenic origin is limited, and that the chemical form of the metals (rather than, as previously assumed, their concentration) may be the controlling factor in determining the unfavourable ecological consequences. This incident also showed the need for improved methods of analysis of trace metals (TM) in natural media. A surprising trend has been recently reported in trace metal analysis: as the sensitivity and the selectivity of the analytical methods improve, the concentration of TM in the natural medium appears to decrease (by several orders of magnitude in some cases) in spite of the concurrent increase in industrial effluent levels. This observation has cast serious doubts on the validity of analytical results. Only very recently have truly reliable analytical data been obtained: these are quoted below in the appropriate sections.

The aim of this review is to generalise published information on the chemical forms of mercury, cadmium, and zinc in natural aqueous media: water (data for sea water are discussed, in part, in Refs.3 and 4), suspended and colloidal particles, sludge deposits, and the biota. Data on the toxicity and on biological conversions of trace metals are also discussed. With very few exceptions, existing analytical techniques are inadequate for the determination of the distribution of chemical forms of the TM in natural media, because the concentrations involved are exceedingly small. We shall therefore devote a special section of this review to a discussion of the chemical properties of mercury, cadmium, and zinc in aqueous solutions, in order to explain the chemical behaviour of these trace elements in nature. Many models have been proposed to account for the distribution of dissolved TMs in natural waters, but they have not been confirmed experimentally. Difficulties in interpretation arise from uncertainties in the stability constants of the complexes between the TM and some ligands, and also from the lack of reliable activity data for the reacting forms. Therefore we shall only mention the most recent models, with the most accurate values of these parameters.

To keep the length of the review within bounds the discussion of some topics (geochemistry, bio-inorganic chemistry, and hydrology) is short, or even fragmentary. For the same reason we have failed to mention many publications in spite of their direct relevance to our topic; the list of references would otherwise have been at least twice as long. Only the most recent research papers and review articles have been included.

† A historically as opposed to biologically related group of plants and animals sharing a common environment.

II. SOME CHEMICAL PROPERTIES OF MERCURY, CADMIUM, AND ZINC IN AQUEOUS SOLUTIONS

Mercury, cadmium, and zinc are typical ("non-transition") metals, because they do not show variable valency and they do not form compounds with an unfilled *d*-shell. They do not form carbonyl or olefin complexes (which are characteristic of transition metals), and they do not show the ligand field stabilisation effect. The failure to oxidise these metals to the tervalent state arises from the very high value of their third ionisation potential, and also from the high solvation energies or lattice formation energies needed to stabilise this state.

Although these metals are classified together in subgroup IIb, the chemical and physical properties of mercury (both in the elementary state and in its compounds) are markedly different from those of cadmium and zinc. Whereas the latter are electropositive metals, mercury has a high ionisation potential and a high oxidation potential, and it is chemically rather inert. The chemical properties of Hg, Cd, and Zn are discussed in detail in Refs.5 and 6. All three metals (especially, mercury) are low-melting and fairly volatile. Mercury has a vapour pressure of 1.3×10^{-3} mmHg at 20 °C, and its solubility in water is 58.8–63.9 μg litre^{-1} at 25 °C, increasing from 19.2 to 368 μg litre^{-1} between 5 and 60 °C in accordance with Henry's law (with a heat of dissolution of 5.3 kcal mole^{-1}).[7] In hydrocarbons and in ethers the solubility of mercury is over an order of magnitude greater than in water[8].

In dry air at ordinary temperature all three metals are practically unaffected (mercury reacting exceedingly slowly), but on being heated they form oxides, though at temperatures above 400 °C mercuric oxide dissociates into its elements. Cadmium and zinc do not liberate hydrogen from water, and in moist air they are quickly covered by an oxide film which protects them from further oxidation. Cadmium plating offers better corrosion protection than zinc plating or nickel plating. All these metals react with sulphur, halogens, etc.: the metallic properties become less marked on going from Zn to Hg, the heats of formation of all the compounds decreasing in that sequence[6]. Mercury reacts with many transition metals and some typical metals to form amalgams, which can have a definite composition (for example, Hg_2Na). The most typical coordination numbers of Hg, Zn, and Cd are 4, 4, and 6 respectively.

Cadmium and zinc cannot exist in aqueous solutions in the univalent state, whereas mercury forms the Hg_2^{2+} ion in which the two atoms are bivalent though the pair is electrochemically univalent and does not undergo electrolytic dissociation. The Hg_2^{2+} ion is related to other oxidation forms of mercury by the reversible disproportionation reaction $Hg_2^{2+} \rightleftharpoons Hg^0(l) + Hg^{2+}$, for which $E^0 = -1.31$ V and $K = [Hg^{2+}]/[Hg_2^{2+}] = 6.0 \times 10^{-3}$, and in which the equilibrium is strongly shifted towards the left. However, in the presence of strong complexing agents (forming strong covalent bonds), of strong oxidising agents, or in alkaline solutions, the equilibrium is shifted almost irreversibly towards the right. The Hg_2^{2+} ion has a low complexing power and it does not form covalent bonds with other elements: as a result, it cannot form metal–organic derivatives[5].

The high stability of the M^{2+} ions in aqueous solution is due to two effects. The first is their tendency to form covalent rather than ionic bonds, especially mercury, many of whose compounds are low-boiling and soluble in organic solvents more readily than in water, and differ from true salts in this respect. The second important property of these ions is their tendency to form complexes with many ligands, the Hg complexes being significantly more stable than those of Cd and Zn.[5,9] The hexa-solvates $M(H_2O)_6^{2+}$, with an octahedral structure, are formed in solution according to an X-ray diffraction study[10] of Hg^{2+}; their heats of solvation lie in the sequence Zn ≫ Cd > Hg. The enthalpy of solvation is much greater for ZnX_2 and CdX_2 (where X is a halogen) than for HgX_2, in keeping with the much stronger interaction between the water molecules and the ion in the case of cadmium and zinc. As a result, the Zn and Cd salts have a tetrahedral or octahedral structure in solution, with water molecules coordinated like those of other ligands, whereas the mercury salts have a linear structure and are very weakly solvated[11]. It is assumed that HgX_3^- ions (where X = Br, I) form a flattened pyramid in solution, whereas HgX_4^{2-} ions form a regular pyramid and CdX_4^{2-} form a regular tetrahedron (as shown by X-ray diffraction results in the case of CdI_4^{2-}).[10,12]

In aqueous solution the degree of dissociation of MX_2 (where X = halogen) falls in the series Zn > Cd ≫ Hg, the mercury halides being ~99% in the form of molecules. The form of the metal is very sensitive to concentration. Thus, $ZnCl_2$ can exist as $Zn(H_2O)_6^{2+}$, $ZnCl^+(aq)$, $ZnCl_2(aq)$, and $ZnCl_4(H_2O)^{2-}$ ions, with out any $ZnCl_3^-$ or $ZnCl_4^{2-}$ ions on the evidence of Raman spectral data[5], whereas CdX_2 exists as Cd^{2+}, CdX^+, CdX_2, CdX_3^-, and CdX_4^{2-}.[5,6] In concentrated solutions of $HgCl_2$ (with $c_{Hg} \geq 1$ *M*) containing a large excess of Cl^- corresponding to a molar ratio Cl/Hg ≥ 4.5 the predominant ion is $HgCl_4^{2-}$, but at $c_{Hg} \geq 0.5$ *M* and a molar ratio Cl/Hg ≅ 3 we find poly-nuclear complexes of the type of Hg_2Cl_4, $Hg_3Cl_{8,3}$, etc.[12] At molar ratios X/Hg < 4 (X = Br, I) HgX_3^- complexes are formed, whereas dilute solutions of HgX_2 contain HgX^+, HgX_2, HgX_3^-, and HgX_4^{2-}, but no poly-nuclear complexes (according to X-ray diffraction and Raman spectral data)[13].

It is believed that the great variety of cadmium forms (and, to some extent, of zinc and mercury forms) is due to self-complexing, for example by the reaction $3CdI_2 \rightleftharpoons Cd(CdI_3)_2$, which drastically lowers the concentration of Cd^{2+}. We note that these reactions take place even in very dilute solutions. At a 0.01 *M* concentration the relative amount of the various cadmium halide forms decreases in the series[6] $CdX^+ > Cd^{2+} \gg CdX_2 \gg CdX_3^- \gg CdX_4^{2-}$.

The ratio of the various forms depends also on pH and concentration. At pH 5 only Cd^{2+} ions are present, but at higher pH values colloidal forms are present together with their ionic and molecular hydrolysis products. In solutions of concentration $\leq 5 \times 10^{-7}$ *M* many pseudo-colloids are formed by the adsorption of $CdOH^+$ and $Cd(OH)_2$ on colloidal impurities, but at pH ≤ 7 and Cd^{2+} ion is predominant whereas at pH 8–10 the predominant species is $CdOH^+$. In solutions of 5×10^{-6} *M* concentration the hydrolysis products polymerise with formation of colloidal $Cd(OH)_2$ or of basic salts[14].

Mercury forms metal-organic compounds of the R_2Hg and RHgX type (where R is an organic radical and X is an inorganic or organic acid residue). The reactivity of these compounds is strongly dependent on the nature of R and X: they are very stable towards water and air (differing in this respect from the corresponding cadmium and zinc compounds[5,15]) because of the very low affinity of mercury for oxygen rather than because of the strength of the Hg–C bonds, which are rather weak (13–52 kcal mole^{-1}, depending on R).[5] Thus, Me^2Hg is stable for about one day in a saturated acid solution or in a 1 M solution of KOH at 85 °C, and it is resistant to photolysis with λ > 290 nm even in the presence of photosensitisers (acetone and singlet oxygen). At 10^{-4} *M* concentration MeHgX (X = Cl, OH) and $MeHg^+$ are photochemically stable for 17 h, but for X = Br, I the compounds are degraded by 10 and 90% respectively in 3.7 h (according to u.v. spectral data); at pH 5 the acidolysis half-life of Me_2Hg is 33 h.[16] Phenylmercury compounds decompose under irradiation with a quantum yield of 0.2–0.3, which is independent of pH. The

decomposition is accelerated by adding photosensitisers with a triplet state energy ≥80 kcal mole^{-1}. The photolysis half-life of these compounds and of Ph_2Hg is 17 and 8.5 h respectively[17]. Me_2Hg evaporates from aqueous solution 2.3 times more slowly than mercury vapour[16], probably because of its higher solubility (3.0 g litre^{-1} at 20 °C).[18]

After lengthy exposure to air, light, and heat the mercury-organic compounds undergo abiotic degradation, with oxygen attack by a free-radical mechanism to give both addition and degradation products[19]: $R_2Hg + O_2 \rightarrow RHgOR$ and $(C_nH_{2n+1})_2Hg + O_2 \rightarrow C_nH_{2n+1}OH + C_nH_{2n}O + Hg^0$. In u.v. light they are decomposed by the same mechanism but to free radicals and mercury: $R_2Hg \rightarrow R^{\cdot} + RHg^{\cdot} \rightarrow R^{\cdot} + Hg^0$.

An important reaction of this type of compound is the reversible symmetrisation reaction $2RHgX \leftrightharpoons R_2Hg + HgX_2$. The equilibrium is shifted towards the right by adding symmetrising agents (iodides, amides, cyanides, aluminium or magnesium oxide, etc.): this effectively removes the inorganic mercury by complex formation, precipitation, or reduction[19]. However, we should note that in aqueous solutions precipitants and sulphur compounds do not act as symmetrising agents[20]. Nevertheless organic mercury has a much lower coordinating power than inorganic mercury. Only the following complexes with simple ligands have been described: $MeHgX_2$ (where X = Br, I, Cn)[21,22], and $RHgX_3^{2-}$ (where X = I and SCN, but not Cl and Br). The $MeHg(SCN)_3^{2-}$ molecule forms a distorted tetrahedron, with two very weak Hg–SCN bonds[23]; $MeHg^+$ exists in water in the forms MeHgOH, $MeHgOH_2^+$, $(MeHg)_2OH^+$, and $(MeHg)_3O^+$, which are mutually related by reversible acid–base and self-association reactions. The last of the above forms has a low stability constant: $K = 0.3–0.7$ (according to titration curves and to PMR and Raman spectra)[21,23,24].

Alkylmercury, like inorganic mercury, forms a much stronger bond with sulphur atoms than with nitrogen, oxygen, or halogens. This effect is clearly shown by the values of log[MeHgX] in water (21.2, 9.37, 7.25, and 5.25 for $X = S^{2-}$, OH^-, NH_3, and Cl^- respectively[23]), and also by the shift of electron density from the ligands towards the mercury in complexes of the $HgY_2.XCH_2CH_2X$ type (Y = Cl, Br, I; X = OMe, SMe, NMe_2) indicated by NMR measurements on the halogen nuclei, which show a decrease in complex forming power in the series S >N >O.[25]

The very insoluble compounds HgS and $(MeHg)_2S$ give rise to the soluble species HgS_2^{2-}, $HgSH^-$, and $(MeHg)_3S^+$ in the presence of an excess or deficit of sulphide ions[26]. The latter dissociates in water by the scheme

$$(MeHg)_3S^+ \rightleftharpoons MeHg^+ + (MeHg)_2S \rightleftharpoons MeHg^+ + MeHgS^- \rightleftharpoons MeHg^+ + S^{2-}.$$

The K_{diss} values for the above steps are given[21] as 10^{-7}, 10^{-16}, and 10^{-21} respectively. In spite of the high affinity of mercury for sulphur, methylmercury is not decomposed by active thiols in water, unlike phenylmercury which undergoes the reaction[20] $Me(Ph)HgCl + RSH \rightarrow MeHgSR$ or RSHgCl: however, it is volatilised in the presence of H_2S, probably with formation of Me_2Hg.[27]

It has been shown that Hg_2^{2+} can form complexes in water with aniline (of composition Hg_2A^{2+}, where A is a monodentate ligand),[28] with organic acids (Hg_2A^+ and Hg_2A_2),[29] and with polyphosphates and dibasic acids ($Hg_2L_2^{-2q+2}$ and $Hg_2L(OH)^{-q+1}$, where L^{-q} is an anion)[30]; some of these complexes are unstable towards disproportionation. Complexes of Hg^{2+} with amines[28] (of composition HgA_2^{2+}) and with organic acids[29] (of composition HgA^+ and HgA_2) have been described, but the formation of 5-, 6-, or 7-membered chelate rings with *O*-substituted carboxylic acids could not be detected.

PMR spectra have been used to demonstrate the formation in aqueous solution of compounds of methylmercury with amines ($MeHgA^+$) and with organic acids (MeHgOCOR), stable at pH 7.5–9.5 and 0.5–13.0 respectively. A detailed description of the interaction of $MeHg^+$ with various ligands is given in Ref. 23. The existence of $[(MeHg)_2OCOMe]^+$ is also suggested[31].

Hg^{2+} is readily alkylated by organic compounds undergoing photolysis. Thus, mixtures of mercuric chloride with small amounts of acetic acid, methanol, or ethanol give MeHgCl (mixed with EtHgCl in the case of propionic acid). The same product is obtained from α-aminoacids of the alanine and leucine type, but not from RHgCl, which suggests that $Me^{\cdot}$ radicals are formed from the acids and methylate the mercury[32]. The yield of methylmercury chloride is very high during the photolysis of mercury acetate, which is reduced as far as the Hg_2^{2+} state in the presence of Cl^-.[33]

Mercury can be easily methylated also by exchange reactions with silicon-, tin-, and lead-organic compounds[34]. These reactions, described by the equation $Me_3E^+ + Hg^{2+} \rightarrow MeHg^+ + Me_2E^{2+}$, go to completion. For E = Sn, Pb the reaction rate can vary by 4–5 orders of magnitude depending on the salinity and the ionic strength of the solution. On the other hand, the arsenic analogue forms metallic mercury[35]: $Me_3As + Hg^{2+} \rightarrow Me_3As^{2+} + Hg^0$.

In the presence of the Hg^{2+} ion many aromatic compounds are easily mercurated by the reaction $Hg^{2+} + C_6H_5X \rightarrow XC_6H_4Hg^+$, accompanied by the formation of labile complexes between the reaction products and Hg^{2+}.[36]

III. CHEMICAL FORMS OF MERCURY, CADMIUM, AND ZINC IN NATURAL WATERS

Natural waters (NW) are complex solutions of different substances. Their chemical composition is extremely varied: they are conventionally classified according to mineral content into fresh waters, brackish waters, sea waters, and brines, with total ion concentrations of < 1.0, 1–25, 25–50, and >50 g kg^{-1} respectively.[37] However, this classification ignores all compositional differences.

The main types of NW are atmospheric precipitation, subterranean waters, and the waters of rivers, lakes, reservoirs, seas, and oceans. The mineralisation of atmospheric precipitation over dry land is usually 10–20 mg litre^{-1} (< 5 mg litre^{-1} for water in clouds), whereas in subterranean and in lake waters it varies from a few tens of mg litre^{-1} to 650 and 350 g kg^{-1} [mg kg^{-1}? (Ed.of Translation)]. According to chemical composition, NW can be classified into five groups: 1) the ion present at the highest concentration (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}); 2) dissolved gases (O_2, N_2, CO_2, H_2S, etc.); 3) biogenic materials (nitrogen, phosphorus, and silicon compounds); 4) trace elements (compounds of all the other elements); 5) organic compounds[37]. The arbitrariness of this classification is evident. For example, Na, Ca, and Fe can be assimilated by living organisms as well as the biogenic elements; also, the concentrations of the biogenic elements are often lower than those of the trace elements.

Most of the Earth's rivers show a low (< 200) or an intermediate (200–500 mg litre^{-1}) degree of mineralisation. High (500–1000) or very high (>1000 mg litre^{-1}) mineralisation of river water is seldom found. However, the chemical composition of river waters is far from uniform, especially along the length of the river (with a smaller non-uniformity across the width of the river and a negligible non-uniformity in the depth), arising from the inflow of tributaries, seepage of subsurface waters, and the uncontrolled timing of the various water flows along the length of the river[37].

Sea (and ocean) waters have a time-independent composition, uniform in different parts of the ocean as well as in depth. In the open ocean the quantitative relationship between the concentrations of the main ions is always constant, irrespective of absolute concentration. This is a fundamental rule in the chemistry of ocean waters. The constancy of the composition of oceanic waters can be perturbed only in the coastal regions, where decreasing salinity is found, and in land-locked seas, where the salinity (S) is usually low and the exchange of water with the ocean is hindered. Sea water shows another distinguishing feature as a chemical environment: a high hydrostatic pressure.

Mercury, cadmium, and zinc are present in NW at concentrations below 1 mg kg^{-1} (1 ppm), and therefore they can be classified as trace metals (TM). However, the true concentrations of TM in NW have only recently been determined[38,39], and found to be at least an order of magnitude lower than previously reported. Precise measurements of [TM] concentrations require careful attention to purity in all stages of the analysis, from sampling to end-determination, and the analytical conditions are very strict. For example, specially air-conditioned premises from which all metal surfaces are excluded are recommended[38]. Water samples for the determination of TM in hydrochemistry are usually filtered through a membrane with a pore diameter of 0.45 μm: this is done in order to compare NW having different concentrations of suspended particles (on which the TM are adsorbed, or chemically bound). These analyses yield the concentration of dissolved TM, whereas unfiltered samples give the total concentrations.

In fresh waters (Alaska snow) the concentration of Zn, Cd, and Hg was found[40] to be 1.07–1.67, 0.08–0.22, and ≤ 0.005–0.026 μg $litre^{-1}$ respectively. The concentration of Hg in ice cores was ~0.01 μg kg^{-1}, varying between 0.002 and 0.019 μg kg^{-1} in the period 1727–1971.[41] In subsurface waters the concentration of TM is strongly dependent on the location and on the sampling time within a particular month, variations as high as 10–100-fold being reported[42]. In the Mississippi estuary# the concentration of Hg was found[43] to be 0.05 μg $litre^{-1}$, and in the fresh river water 0.01–0.039 μg $litre^{-1}$.[44–46] Of the various forms of mercury, only $MeHg^+$ was determined, though it accounts for only a small part of the dissolved mercury. In the Great Lakes < 2.4×10^{-4} μg $litre^{-1}$ was found; in some other lakes of Canada 5–7×10^{-4} μg $litre^{-1}$; in the Mississippi estuary and in the Everglades less than 2 and 1% respectively[43]. The concentration of Cd in two rivers of Australia[47] was 0.02–0.30 μg $litre^{-1}$, and at the mouth of the Amazon[48] 0.067 μg kg^{-1}.

The mercury content of the surface water in the Atlantic and the Indian Ocean is 0.008–0.0335 and 0.0112–0.0201 μg $litre^{-1}$ respectively, in the China Sea 0.016–0.0284 μg $litre^{-1}$, and near the shores of Great Britain 0.0061–0.028 μg $litre^{-1}$.[49–51] The concentration in unfiltered water in the Atlantic Ocean increases with depth (0–4030 m) from 0.03–0.04 to 0.142 μg $litre^{-1}$.[52] In the Arctic Sea the concentration of Cd is 0.11 μg $litre^{-1}$,[53] in the Atlantic Ocean 0.04 μg $litre^{-1}$ [54] and 0.060 μg kg^{-1},[55] and in coastal waters < 0.05–0.8 μg $litre^{-1}$.[54] In the Pacific Ocean the concentration of Zn and Cd increases with depth (0.2–2950 and 0.3–5500 m respectively) from 0.01 to 0.6 μg $litre^{-1}$ [41] and from 0.1 to 1.1×10^{-9} mole kg^{-1},[48] indicating absorption of these metals by living organisms near the surface and regeneration at great depth from biological deposits under pressure[39,48]. The same explanation applies to the distribution of Cd (< 0.01–0.025 μg $litre^{-1}$) in the Sargasso Sea[56]. The rate of vertical transfer of Zn by biologicial means from pelagic organisms to those of the benthos§ is calculated to be much lower than the rate of transfer through excreta, and is approximately two years[57]. On the whole there is no evidence of contamination of the waters of the open oceans by Hg, Cd, and Zn.

The concentration of metals in NW is highest in a microscopic surface layer (or film) in which micro-organisms, plankton, organic compounds, and biogenic elements are also concentrated. In comparison with the underlying layers the concentration factor of the micro-layer can be as high as 100 or 1000. In these circumstances correct sampling becomes a fundamental (and so far unsolved) problem. A film 100 μm thick is usually taken, but this is too thick in comparison with a monolayer of organic and inorganic molecules (5–30 × 10^{-3} μm). Therefore the concentration factor in reality is very much greater than the measured factor. It is important to note that in surface layers from sea water the metals are bound exclusively to organic substances, the concentration of inorganic forms being the same as in the underlying layers of surface waters[58]. Since these layers can form an easily collected foam in the wind, the concentration factor for foams should be very much higher than for layers collected by submerged metal gauzes. Factors of 408 and 300 for Zn and Cd respectively were obtained for the foam from a lake in the USA.[59]

The total metal content of the ocean is believed to be held constant by the balance between the rates of addition and of removal. The mean residence time of metals in the ocean is determined from the rate of precipitation into the bottom deposits or from the rate of supply from the rivers to the ocean. These times, which are an indication of the relative reactivity of Hg, Cd, and Zn, are 26000 and 42000 years[60], 7700 and 92000 years, and 7800 and 18000 years[61] respectively.

Table 1. Estimated average concentrations of the main inorganic components dissolved in river and sea waters[62].

Component	River water		Sea water (S=35‰)	
	concn, mg $litre^{-1}$	proportion of total dissolved solids, %	concn. mg $litre^{-1}$	contribution to S, %
Na^+	6.3	5	10 770	31
K^+	2.3	2	399	1
Mg^{2+}	4.1	3.5	1 294	4
Ca^{2+}	15	12.5	412	1
Fe	0.7	<1	<0.01	—
Cl^-	7.8	6.5	19 340	55
SO_4^{2-}	11.2	9	2 712	8
HCO_3^-	58.4	49	140*	0.4
Silicon	13.1**	11	<0.1—>10***	—

* Inorganic carbon as HCO_3^-.
** As SiO_2.
*** Value depends on location and depth.

The dissolved forms of TM in NW are largely determined by the nature of the main ions and of the organic substances present. Estimates of the average concentrations of the main inorganic components of river and sea waters[62] are given in Table 1. Among the main ions of sea water, making a significant contribution to the salinity with concentrations

Funnel-shaped mouth of a river, widening out towards the sea.

§ From organisms swimming or passively drifting in the sea to those living on (or in) the bottom deposits, or moving along the sea bottom.

greater than 1 mg kg^{-1}, should be included boron compounds, Sr^{2+}, Br^-, and F^-: their concentrations are given[69] as 4.5, 7.9, 67.3, and 1.3 mg kg^{-1} at a salinity of $S = 35‰$.

Depending on the analytical method and separation technique used, several schemes have been proposed for classifying the chemical forms of metals in NW (see, for example, Ref.64). It is convenient to subdivide the forms of metals into: simple hydrated ions (M^{2+}.aq), simple compounds and complexes with inorganic (MCl_4^{2-}, MCO_3) and with organic ligands (aminoacids and citrates), stable compounds and complexes with inorganic (MS, $MSiO_3$) and with organic ligands (M-humates), and metals adsorbed by inorganic colloidal particles (M^{2+}–$Fe_2O_3.nH_2O$, M^{2+}–$MnO_2.nH_2O$, M^{2+}–clay) and by organic colloidal particles (M^{2+}–humic acids, M^{2+}–organic detritus).[65] Because of the specific chemical properties of mercury, to these forms of M^{2+} we should add $MeHg^+$ and Hg_2^{2+}, and also Hg^0 (the solubility of mercury in sea water at 30 °C obeys Henry's law and increases from 17.2 to 69.7 μg $litre^{-1}$ between 5 and 30 °C)[7] and Me_2Hg (whose solubility in sea water decreases from 2.84 to 1.88 g kg^{-1} between 0 and 26 °C).[18] The methods used to determine the forms of metals in NW are discussed in Ref.65. In particular, it is shown that Cd and Zn are present as M^{2+}.aq, as well as hydroxyl and chloride complexes (in the case of sea water).[53] We note that $^{65}Zn^{2+}$ is not transferred to the organic fraction even one year after being added to sea water[53]. No isotope exchange takes place between Hg^{2+} and MeHgCl in fresh waters[67].

NW always contain very small amounts of soluble organic compounds (SOC) consisting mainly (up to 80%) of highly oxidised and biologically stable polymeric compounds similar to the humus materials (HM) extracted from soils. The concentration of SOC in fresh waters is usually 1–10 mg $litre^{-1}$,[68] but in sea waters it is only 0.5–1.0 mg C $litre^{-1}$,[69] because of the dilution and flocculation which occurs at the boundary between fresh water and sea water[70]. The rest of the SOC consists of a mixture of polypeptides, polysaccharides, amino-acids, fatty acids, hydrocarbons, vitamins, and many other compounds. The low concentration of these materials (0.008–0.5 mg $litre^{-1}$ in the case of amino-acids[71]) is the result of bio-degradation. It makes identification very difficult: for example, in the case of sea water only ~10% of the compounds have been identified, since only a few compounds are present at a concentration $>10^{-6}$ M.[69] The problem of SOC in sea water is specially discussed in Ref.72. In polluted rivers, on the other hand, ~100 different compounds have been identified, including organic solvents and poly(ethylene glycols).[73]

Humus materials are transferred to NW through the fractional extraction of organic compounds from soils by atmospheric precipitation. They are subdivided into three components: humic acids (HA), which are soluble in basic solutions, fulvic acids (FA), which are soluble in both basic and acid solutions (and produce a yellow colour in fresh waters and subsurface waters[68]), and insoluble humus material. The distinction between these three classes is not always clear, and differences may arise from variations in elemental composition, acidity, degree of polymerisation, and molecular weight (MW).[74] In fresh waters FA and HA have MW of 300–2000 and 5000–100000 respectively[68]. The average MW of unfractioned humus from water is ~1000.[70]

The structure of humus materials is unknown. They are high-molecular poly-electrolytes of indeterminate composition. However, it is usually assumed that HA molecules consist of benzene and heterocyclic rings (probably condensed), with di- and trioxy groups, connected by CH_2-, O-, NH-, –N-, and S-groups to which are attached side chains with various functional groups. FA are believed to differ from HA by having a much greater proportion of functional (especially carboxylic acid) groups and aliphatic carbon, and a smaller proportion of aromatic carbon[68,74]. HA from soils have been shown by the NMR method (^1H and ^{13}C) to contain up to 65% of aromatic and carboxylate carbon and a large number of aliphatic OH groups: their structure is quite different from that of coal and lignin[75]. The chemical characteristics of humus from water and of sea-water FA are discussed in Refs.76 and 77.

Humus materials combine with metal ions, take part in cation exchange, contain free radicals, and adsorb metal hydroxides, proteins, insecticides, alkanes, etc. They can adsorb metal ions (up to 1–17% by weight).[68] Being stable organic free radicals[68], HA can reduce Hg^{2+} to Hg^0 in aqueous solution at pH 6.5–8.2 by a first-order reaction ($k = 0.009$ h^{-1}).[78]

The chemical nature of the combination of metal ions with HA and FA is not understood at present. It has been suggested that binding occurs through all the ion-forming functional groups, and that chelation plays an important role, as in the case of salicylic acid and pyrocatechol.[74,79] However, the analogy is not clear: for example, in HA at least 1/3 of the phenol groups has been shown not to be in the *ortho*-position with respect to the carboxyl groups[80], and the nature of the remaining phenol groups is uncertain. The metals may be combined in a tetrahedral or an octahedral coordination, in which they are fairly stable towards complex formation and reduction (as demonstrated by ESR and Raman spectra in the case of Fe^{3+}).[81] Two complex formation centres have been found in HA, with K values differing by an order of magnitude[82].

Because of the difficulty of identifying and quantitatively determining all the organic ligands dissolved in NW, the concept of the complex-forming power of the NW itself has been proposed. This quantity is a measure of the ability of the NW to form complexes with (or mask) a given metal ion. Methods of determining it are discussed in Ref.79. Values of $1–7 \times 10^{-7}$ M have been reported[83] for Cu^{2+} in fresh waters, whereas in sea water the values for Cu^{2+} and Pb^{2+} are 10^{-8}–3×10^{-7} M[53,65] and 3.2×10^{-7} M[53] respectively. Biological methods of determining complex-forming power have also been proposed[84]. These results include only a small fraction of the real complex-forming ability of the NW, since most of the reactive centres in the organic ligands are already occupied by strongly bound metals such as Fe^{3+} and Al^{3+}. For example, 7 mg $litre^{-1}$ of FA contain ~20 μmole $litre^{-1}$ of potentially reactive sites, but typical values of the measured complex-forming power[83] lie in the range 0–2 μmole $litre^{-1}$.

In NW the extent to which trace metals are combined with SOC depends on the concentration of the TM, on competition from other ions present in higher concentrations, and on pH. However, the results of the measurements can be strongly influenced by the chosen method. Thus, several workers find that most of the Zn,[85] Cd,[86,87] and Hg[44,85,87] in fresh waters is combined with SOC, whereas Florence[88] reaches the opposite conclusion for the first two of these metals. In coastal sea waters Hg[43,44,50] and Zn[53] (but not Cd) will also be found preponderantly in the organic fraction, though the effect is not observed in the open ocean[51]. FA combine with metals very strongly[43,87,89], but the complex-forming power of HA depends on their origin[90], on the pH, and on the presence of Ca^{2+} and Mg^{2+}.[91] The stability of the Zn^{2+} and Cd^{2+} complexes decreases in the sequence HA $>OH^-$, HCO_3^-, CO_3^{2-} > glycine[91]. FA from soils, with an average MW of 2775, forms Cd complexes of 1 : 1, 2 : 1, and 3 : 1 composition having stability constants $K = 10^{6.0}$, $10^{10.7}$, and $10^{15.4}$ respectively[79] at pH 7.7.

By using the gel filtration method at pH 8.0 it was found[92] that the stability of the complexes formed by HM with particular trace metals depends on the origin of the HM: $\log K = 4.83$–5.87 for Zn, 4.57–4.95 for Cd, and 18.0–21.3 for Hg. On the

whole the stability of metal–HM complexes follows the Irving–Williams stability series for metal chelates: Mg < Ca < Cd ≅ Mn < Co < Zn ≅ Ni < Cu < Hg.[92]

Because of the exceedingly low concentration of TM in NW their chemical form cannot be established by existing analytical techniques, but the effect of various equilibria on the chemical form is discussed in Refs.69 and 93. Therefore, equilibrium concentrations are calculated by using models relying on arbitrary values of the stability constants (β) of the complexes formed with inorganic ligands in conjunction with the analytically determined concentrations of the TM. However, very different β values may be used for a given complex by different workers, leading to large differences in composition and relative abundance of the various forms. For example, by inserting into the model more accurate values of β for $Zn(OH)_2$ and $ZnCO_3$ the calculated distribution of the main forms of zinc in sea water ($S = 35‰$, pH 8.1) changed from 60% $Zn(OH)_2$, 17% Zn^{2+}, 7% $ZnCl^+$, and 5% $ZnCO_3$ to 47% Zn^{2+}, 20% $ZnCl^+$, 10% $ZnCl_2$, and 10% $ZnSO_4$.[92] Other calculations suggest that in fresh waters at pH 5–9 the main forms of $MeHg^+$ are $MeHgS^-$, $(MeHg)_2S$, and MeHgSR, or (in the absence of sulphur compounds) MeHgOH and MeHgCl.[94] Sea water of salinity $S \cong 10‰$ and pH 8.2 contains 11.8% $HgCl_2$, 22.8% $HgCl_3^-$, and 64.5% $HgCl_4^{2-}$,[95,96] but under reducing conditions the main forms of zinc are $Zn(SH)_3^-$ and $Zn(SH)_2$.[97] In estuarine waters at pH 6.5–9.5 zinc and cadmium are found predominantly in the M^{2+}, MCl^+, and $M(OH)_2$ forms[98], but in fresh waters, allowing for adsorption[99], the predominant form is M^{2+}.

Table 2. Arbitrary stability constants of some inorganic forms of Hg, Cd, and Zn.[92]

Ligand	lg β₁			lg β₂			lg β₃			lg β₄		
	Zn	Cd	Hg	Zn	Cd	Hg	Zn	Cd	Hg	Zn	Cd	Hg
Cl^-	0.40	2.0	7.28	0.61	2.7	14.01	0 53	2.1	14.98	0.20	—	15.76
SO_4^{2-}	2.3	2.3	2.42	—	3.5	3.52	—	—	—	—	—	—
HCO_3^-	1.9	1.8	2.5	—	—	—	—	—	—	—	—	—
CO_3^{2-}	4.8	4.4	6.3	—	—	—	—	—	—	—	—	—
OH^-	4.40	5	10.86	10.0	10.6	12.24	14	10	—	15	10	—

Table 3. Calculated concentrations of the chemical forms of metals in lake waters, mole %.[92]

Component	Free ion	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	OH^-	HM
Mg	98.2	—	0.5	0.5	—	—	0.8
Ca	97 8	—	0.6	0.9	—	—	0.7
Cu	—	—	—	—	—	—	99.97
Zn	88.8	—	0.5	3.1	0.6	—	7.0
Cd	92.8	0.7	0.5	3.0	0.2	0.1	2.7
Mn	90.6	—	0.5	2.9	0.9	—	5.1
Hg	—	—	—	—	—	—	100.0
Ni	69.6	—	0.4	11.1	11.2	—	7.7
Co	76.0	—	0.5	9.6	9.8	—	4.0
	free	Mg	Ca	Cu	Zn	Mn	Ni
HM	75.2	6.4	15.0	0.8	1.0	1.5	0.1

Using improved values of β for the complexes of metals with inorganic ligands (Table 2) in conjunction with experimental values of the stability constants of the complexes with humus materials and of the concentrations of main ions, TM, and HM, and of the total inorganic carbon and carbonate alkalinity and pH, the forms of the metals in lake waters have been calculated (Table 3). We note that >99% of the Hg and Cu is combined in the HM, whereas in the case of the other metals 70% or more is in the form of free cations. On the other hand in sea water >99% of the HM is combined with Ca and Mg, which are present at relatively high concentration, and among the TM only Cu is combined to a significant extent (~10%). The equilibrium forms of the TM have been calculated also as a function of salinity (Figs.1–3).[92] All these calculations ignore the formation of mixed or poly-nuclear complexes, and interfacial reactions.

We should stress that the formation of dissolved chemical forms of TM in NW is determined by several parameters: the pH, the redox potential, the nature and concentration of the TM, of inorganic and of organic ligands, and of colloidal particles (and the accessibility of their surface), and the possibility of interfacial reactions (precipitation, dissolution and sorption, biological and physical processes, etc.). The qualitative and quantitative effects of most of these factors on the chemical forms of dissolved metals are unknown. Therefore we cannot determine the extent to which the calculated forms of metals in NW approach the real distribution, even when very correct models are used in the calculation.

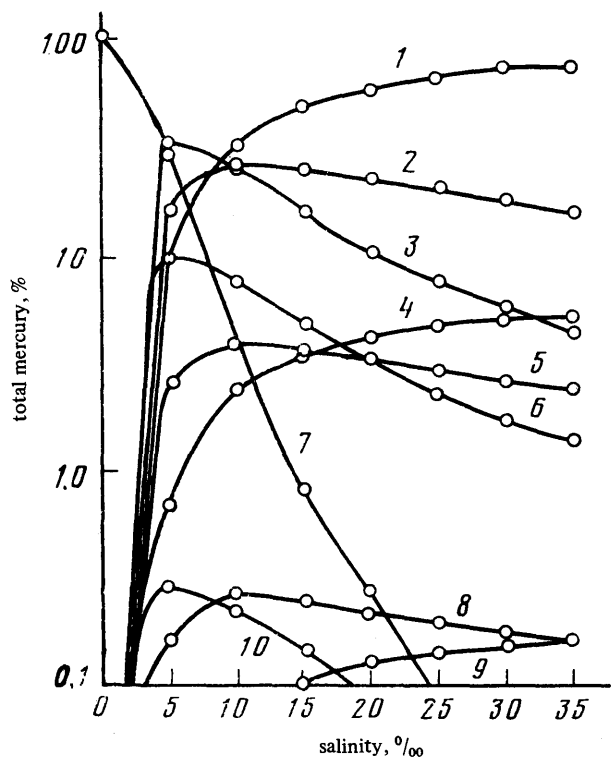


Figure 1. Equilibrium chemical forms of Hg^{2+} in the water of a model estuary[92]: *1*) $HgCl_4^{2-}$, *2*) $HgCl_3^-$, *3*) $HgCl_2$, *4*) $HgCl_3Br^{2-}$, *5*) $HgCl_2Br^-$, *6*) HgClBr, *7*) mercury combined with humus materials, *8*) $HgClBr_2^-$, *9*) $HgCl_2Br_2^{2-}$, *10*) $HgBr_2$.

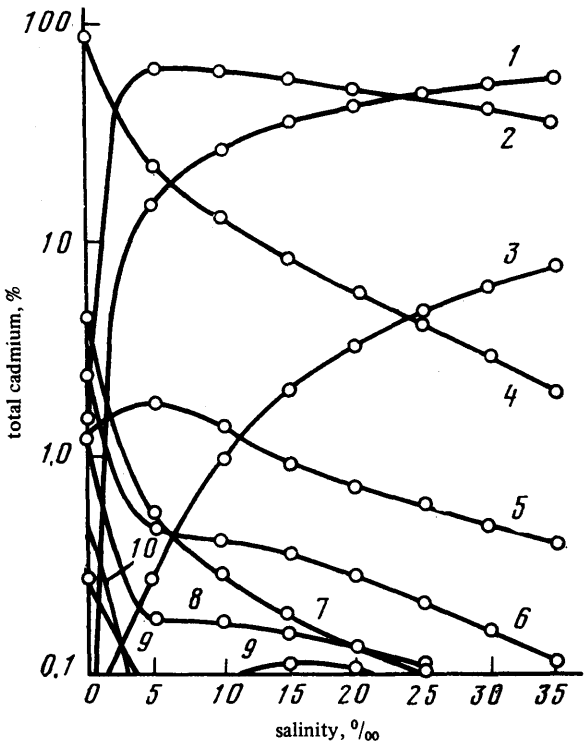


Figure 2. Equilibrium chemical forms of Cd^{2+} in the water of a model estuary[92]: *1)* $CdCl_2$, *2)* $CdCl^+$, *3)* $CdCl_3^-$, *4)* Cd^{2+}, *5)* $CdSO_4$, *6)* $CdHCO_3^+$, *7)* $CdOH^+$, *8)* $CdCO_3$, *9)* $Cd(OH)_2$, *10)* cadmium combined with humus materials.

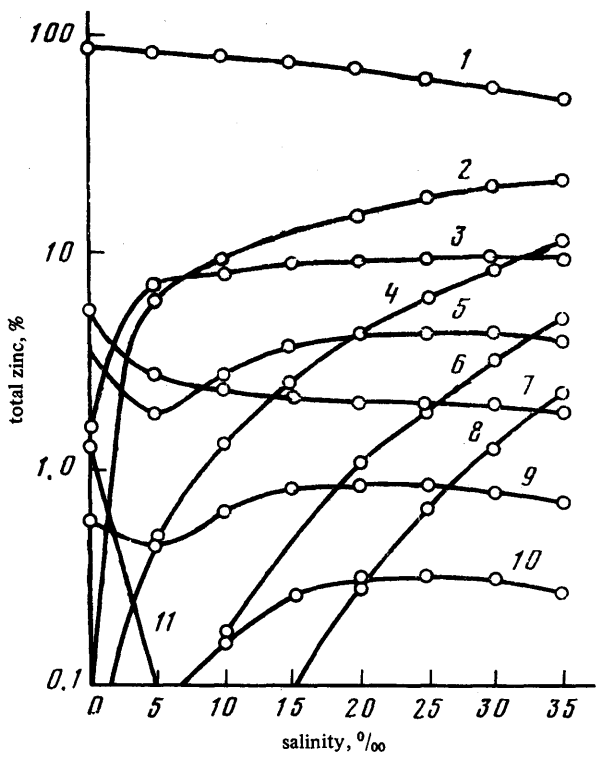


Figure 3. Equilibrium chemical forms of Zn^{2+} in the water of a model estuary[92]: *1)* Zn^{2+}, *2)* $ZnCl^+$, *3)* $ZnSO_4$, *4)* $ZnCl_2$, *5)* $ZnCO_3$, *6)* $ZnCl^+$, *7)* $ZnHCO_3^+$, *8)* $ZnCl_4^{2-}$, *9)* $ZnOH^+$, *10)* $Zn(OH)_2$, *11)* zinc combined with humus materials.

IV. FORMS IN SUSPENDED AND COLLOIDAL PARTICLES

Filtration of any NW through a membrane filter of 0.45 μm pore size produces a small residue of suspended particles (SP). The concentration of SP in the oceans is very much smaller than was previously thought: only 10 μg kg^{-1} at depths >200 m, though in surface waters the concentration varies with the season and can reach several hundred μg kg^{-1}. Most of the particles are 1–10 μm in diameter, a few are >10 μm, and the biological particles can be as large as 1 mm. The size distribution of the SP is usually independent of depth[100].

The majority of SP are particles of biological origin, found near the surface of the ocean[101]; their concentration is often greatest in regions where plankton is most abundant[102,103]. However, detritus forms are the predominant type of biological particle. In surface waters (at depths < 100 m) solid skeletal phases of marine organisms ($CaCO_3$ and SiO_2) account for 25–50% of the mass of SP, and organic substances for 30–70%.[100] The distribution and recycling of SP is particularly influenced by the presence of zooplankton[100,102]. Some of the biological particles are transferred to the sea bottom as fecal pellets[100,101], which account for 99% of the vertical transport of SP at depths >380 m (as compared with only 4% near the surface).[101]

Suspended particles are subdivided into two main groups: biogenic and non-biogenic, each of which consists of two or more subgroups. The first group includes both organic and inorganic materials ($CaCO_3$, $SrSO_4$, opal SiO_2), and the second consists mainly of alumino-silicate particles including clay and anhydrous minerals, but it includes other minerals (quartz, pyrites, dolomite, barytes, titanite, and iron and titanium oxides[103,104]). As the SP sink their inorganic content increases, mainly by the addition of sea salts in proportion to their concentration in sea water[105]. Near the sea bottom large amounts of SP are formed by the re-suspension of silt under the influence of various flows[106]. For example, a sample of SP taken at a depth >5000 m in the Sargasso Sea and consisting of 50% clay, 20% $CaCO_3$, 20% SiO_2, and 5% organic matter had originated mainly from the sea bottom[107].

Large numbers of SP are found in the surface micro-layer and in the foam of NW, producing an enhanced concentration of suspended TM.[59,108,109] For example, enrichment factors of 235 and 800 have been reported for Zn and Cd in lake foams[59]. TM are assumed to be concentrated at the water–air interface by atmospheric precipitation, and by adsorption and transport from the surface layer by air bubbles[108,109] formed by the waves, which are also the main source of aerosol particles containing sea salts[108].

Little is known about the content of TM in suspended particles. In the surface layer of the Pacific Ocean the average concentration of Zn in SP is 220 μg g^{-1};[110] in the Baltic Sea values of 0.006 and 0.99 μg $litre^{-1}$ were obtained for Cd and Zn respectively[111]. Relatively high TM concentrations are found in the fecal pellets of zooplankton, even in comparison with the amounts found in zooplankton itself: Cd (9.6 and 0.74), Zn (950 and 62), and Hg (0.34 and 0.35 μg g^{-1} respectively).[112] When the SP sink to a relatively small depth the metal content does not change significantly[111], but at greater depths there is a marked decrease (to 1.7 and 3.3% of the total concentration for Cd and Zn respectively[113]), the concentration in the case of Cd being lower by a factor of 4 at depths <400 nm.[55]

The concentration of suspended trace metals (especially Zn and Cd) in the ocean is determined by the amount of suspended organic matter[114] with which the TM are combined[103]. The composition and concentration of suspended organic matter have not been adequately studied, but proteins always appear to be present (up to 270 and 32 μg litre^{-1} have been reported for coastal and open waters respectively of the Pacific Ocean[115]). In rivers and lakes the concentration of suspended organic compounds is substantially (6–10-fold) lower than the concentration of SOC.[70] The chemistry, biology, and vertical distribution of SP in the ocean are discussed in Refs. 100–102 and 116, and their role in the detection of TM in Ref. 117.

By far the greater part of the TM transferred to the ocean from rivers is on suspended particles[118]: the proportion can be as high as ~80% (for Zn and Cu)[119] and even 90% (including Zn and Cd) in the Mississippi river[120]. The only exception is mercury, ~80% of which is transported in a soluble form while only 15–19% is found on SP.[121,122] Where fresh waters mix with sea water in estuaries, i.e. where a decrease in the flow rate is accompanied by an increase in salinity and (sometimes) in pH, two opposing processes take place[60,118,123]: 1) settling of the SP, and rapid formation and precipitation of flakes of colloidal particles containing Fe, Mn, Al, P, organic carbon, and HM,[124] accompanied by the coprecipitation of TM; 2) the release of the TM from the SP to the water. The relative importance of these two processes has not yet been determined. In some rivers of Europe[118] and of America the TM content (including Hg and Zn) of the SP decreases as the salinity increases: for example, from 403 to 240 for Zn and from 1.8 to 0.9 μg g^{-1} for Cd.[123] The influence of SP on the distribution of TM in estuaries is discussed also in Refs. 125 and 126.

Because of their rapid initial release, followed by a much slower release, the TM can be in an ionic or a complex form: this happens mainly as a result of breakdown (by oxidation) of the supporting particle[118,127], but it may be due also to desorption caused by dilution[127], stoichiometric exchange of Ca and Mg,[60] or complex formation with organic or inorganic ligands[127].

Trace metals are taken up by SP by adsorption on oxide surfaces[128]: Cd is combined only with Mn, and Zn mainly with Fe.[129] Alternatively, the TM are incorporated into the SP by complex formation, by ion exchange with clay minerals, or by reaction with humus materials[118] or with colloidal organic particles. The degree of combination is very sensitive to pH,[60,130] and can be controlled by chemical reactions at the interface through (for example) redox processes involving the substrate ($Fe^{3+} \rightarrow Fe^{2+}$) or the metal ions[131]. Humus materials can adsorb TM as well as reacting chemically with them: the adsorbed TM are held octahedrally (relatively weakly), they easily form complexes, and they are easily reduced[81].

Colloidal particles of inorganic (hydrated Fe, Mn, and Si oxides, clays, sulphides) or organic origin (HM, residues from living organisms) play an important role in controlling the degree of combination of TM in NW.[65] Inorganic colloidal particles can sorb (or chemically combine with) organic colloidal particles, and therefore they have hydrophilic properties and they oppose agglomeration.[69] It has been suggested[65] that most of the SOC in NW are in a colloidal state. Colloidal particles can combine with Cd, Pb, and Cu to the extent of 15–30, 45–70, and 40–60% respectively of their total content in sea water, but Cd and Pb are found mainly in inorganic forms, and Cu is found also in organic forms.[132] Although the colloidal fraction of TM is classified with the soluble forms the mechanisms by which the metals are combined with colloidal and with suspended particles must be similar.

V. FORMS IN SLUDGE DEPOSITS

Depending on their origin, sludge deposits consist of: 1) a lithogenous fraction (clay minerals, quartz, etc.) formed by soil erosion and usually carried by rivers into the sea; 2) particles of the hydrated Fe_2O_3 type, formed in water by inorganic reactions; 3) a biogenic fraction consisting of inorganic particles of the $CaCO_3$ type, of biological origin, and organic materials including residues from dead biota[60]. They usually have a redox potential of 100–(−400) mV, or 300–600 mV in surface waters, and pH 6.5–7.5.[133]

The upper few centimetres of bottom sludges in estuaries and coastal waters are usually in an oxidised state and are often brown, whereas the deeper layers tend to be in a reduced state, black in colour, and smelling of H_2S. Organic matter, which can account for up to 10% of the bottom sludge (or more), is decomposed by micro-organisms under both aerobic and anaerobic conditions[60]. The resulting humus material has a MW ranging from < 500 to >300000: for most of the HA the MW is >300000, but for the FA the MW is < 500 or >100000–300000 (see Ref. 74).

Sludge deposits showing different levels of contamination may contain the following metal concentrations (expressed as μg g^{-1} of dry weight): Hg from 0.01 to 14.3, Cd from 0.05 to 60, Zn from 3 to 2500.[135] In rivers the concentrations of Cd and Hg are 1.0–9.8[136] and 0.03–1.28[122] respectively, and in the Atlantic the concentrations of Cd and Zn are 0.13–0.21 and 17–134[55] respectively (μg g^{-1} of dry weight). In rivers the biota contains only 0.02% of the total mercury, and the bottom sludge contains ~97%.[122] The fractional amount of $MeHg^+$ in the bottom deposits varies from 0.1 to 2.1%, and is 100 times greater than in the biomass of the river[67]. It is important to note that only a small proportion of the metal content of the bottom sludge can be transferred to the sea by the flow of the river. In the case of mercury, for example, the proportion is ~1% of the total amount of mercury carried by the river[121,122]. However, the concentration of TM in bottom sludges is not uniform. It is highest (by a fairly large factor) in the fractions with the smallest particles[122,137] and in the fractions richest in organic matter[74,122,136,138,139]. The latter fractions are usually found downstream from regions with a highly developed heavy industry, and they are composed of settled SP.[139]

The main components of the organic fraction of free sea sludges are HM, amounting to 40% of the sludge and formed in the marine environment. Marine HA have a very high sulphur and nitrogen content.[140] They combine with TM by cation exchange and complex formation through oxy-, amino-, and thio-groups, and also by surface adsorption[140,141]. The HA are usually formed in the sludge by diagenesis¶, and they leach the TM out of the solid mineral phases[74,140] (a reaction of great importance in geochemical processes). However, the form in which the metal exists in the bottom sludge is determined by various allochthonous interactions and autochthonous processes[142]. Thus, in some sludges the Cu, Zn, and most of the Mo are combined with organic substances, and the Ni and Co with sulphides[140], whereas in others the Mn and Zn are found predominantly in the carbonate phase, the Pb in the hydroxide phase, and most of the Cd can be readily exchanged[142]: in some samples the Cd is found in the carbonate, sulphide, and organic form (80, 10, and < 5% respectively), and >90% of the Zn is in the carbonate and the organic phase in comparable amounts[143], but in other samples the Hg is accumulated in the sulphide phase[144].

¶ The totality of the natural processes by which loose deposits at the bottom of water basins are converted into sedimentary rocks.

The MS sulphides (M = Hg, Zn, etc.) are stable under anaerobic conditions, but under aerobic conditions they are oxidised in proportion to their solubility in water[145]; also, Hg^0 can be oxidised to Hg^{2+} in soils (2–27%) and it can combine with organic substances[146]. The affinity for Hg^{2+} adsorption decreases in the series RSH ≫illite >montmorillonite >RNH_2 >kaolinite >RCOOH >fine sand >medium sand > coarse sand[147]. In contaminated sludge the concentration of the Zn forms decreases in the series organically bound >carbonate >sulphide >adsorbed >exchangeable, and that of Cd in the series carbonate >sulphide >organically bound >adsorbed > exchangeable.[148]

The TM transferred to the ocean by different routes (by the rivers and from the atmosphere, through effluent waters and ship discharges, etc.) always accumulate in the bottom sludges of the coastal areas of seas and lakes. Therefore a core sample of the sludge taken without disturbing the stratification can describe the accretion of TM in a given basin over any period of time up to several centuries. The geochronology of the deposits is determined from the distribution of the radioactive isotopes ^{210}Pb, $^{239+240}Pu$, and ^{137}Cs. In the surface layers of sea and lake deposits near large industrial, mining, and urban regions the concentrations of Cd, Zn, Hg, Pb, Cu, and other TM can be 5–10 times greater than in the layers laid down 50–100 years ago, thus reflecting their anthropogenic origin.[149–153] A historical plot of the vertical Zn and Cd profiles in one of the lakes of the USA[151] is reproduced in Fig.4: we note that the anthropogenic supply of these metals began in ~1910.

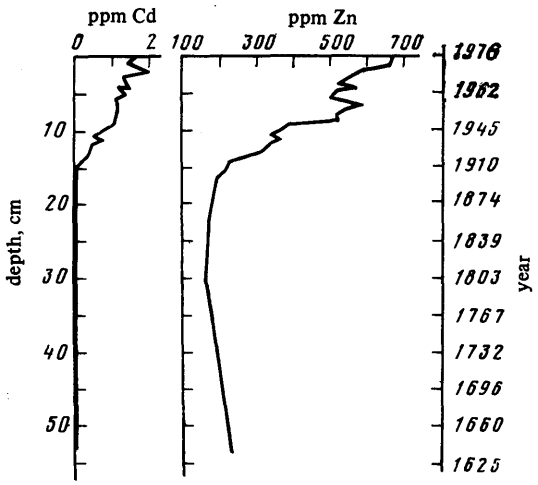


Figure 4. Concentrations of Cd and Zn as a function of depth in the bottom sludge of a lake in the USA.[151]

The sludge waters in contact with the bottom deposits always differ from the water in higher levels because of slow reactions in the sludge, which change the chemical composition of the water[154]. The composition of the sludge waters also depends on the depth of the deposits[155]; their organic content is high (30–800 mg C $litre^{-1}$ in marine sludges[69]), and in fresh water sludges the MW is >300.[74] Sulphide ions and oxygen are the most important components, because they determine the concentration of TM in sludge waters: under reducing or oxidising conditions [TM] can be 1–2 orders of magnitude lower or higher than in sea water.[154,156,157] This effect is ascribed to the formation of complexes with SOC[140] and of insoluble sulphides[60,156,157]. However, we should note that the concentrations of TM under reducing conditions are very much higher than the thermodynamic solubilities of their sulphides. This is due to the enhanced solubility of the sulphides in the presence of organic compounds, or to the formation of the more soluble polysulphides[60,158]. Under oxidising conditions most of the dissolved Hg is present as complexes with organic compounds of MW < 500 or >100000.[158] The most important dissolved forms of Zn, Cd, and Hg in marine sludge waters, calculated by combining experimental results with an equilibrium model[156], are listed in Table 4. However, the model ignores complexes formed by metals with HM, which are very important in the case of mercury.

Table 4. Main dissolved forms of mercury, cadmium, and zinc in the sludge waters of marine deposits at pH 7.5[156] (as % of total concentration).

Oxidising condition		Reducing conditions	
component	content	component	content
$HgCl_4^{2-}$	80.4	HgS_2^{2-}	98.5
$HgCl_3^-$	15.4	Hg (cysteine)	1.2
$HgCl_2$	4.1	$HgS(HS)_2^{2-}$	0.2
$Hg(OH)_2$	<0.1	$Hg(HS)_3^-$	<0.1
HgClBr	<0.1	$HgS(H_2S)_2$	<0.1
$CdCl^+$	56.5	$Cd(HS)_2$	97.2
$CdCl_2$	15.2	$Cd(HS)_3^-$	2.2
$CdCl_4^{2-}$	10.0	$Cd(HS)_4^{2-}$	0.1
$CdCl_6^{4-}$	9.1	$Cd(HS)^+$	<0.1
$CdCl_3^-$	9.0	$CdCl^+$	<0.1
Zn^{2+}	38.1	$Zn(HS)_3^-$	99.2
$Zn(OH)_2$	29.6	Zn^{2+}	0.2
$ZnCl^+$	18.0	$Zn(OH)_2$	0.1
$ZnCl_2$	6.6	$ZnCl^+$	<0.1
$ZnSO_4$	4.3	$ZnCl_2$	<0.1

The direction of the migration of TM in the water–sludge system is determined by the redox potential and by the pH,[156,159] and also by the chemical composition of the sludge waters and of the water in the higher levels[156]. Two opposite points of view on the effect of the redox potential can be defended[159]: 1) the presence of sulphides under reducing conditions will cause precipitation of the TM, but oxidation to SO_4^{2-} will make the TM mobile and transfer them to the supernatant waters; 2) the TM will be solubilised under reducing conditions because of the reduction of the Fe and Mn hydroxides on which the TM are sorbed or coprecipitated under oxidising conditions. It is experimentally found that the extent to which the Fe and Mn become mobile increases as the redox potential is displaced towards reducing conditions, and the mobility of Zn, Cd, Cu, Pb, and Ni increases in the oxidising region, whereas in the case of Hg and Cr the redox conditions appear to be irrelevant. Mobility can be produced by redox reactions, complex formation, dissolution, diffusion, desorption, biological effects, and dynamic processes[156]. For example, TM become mobile when river sludges are mixed with sea water.[160]

VI. FORMS IN THE BIOTA

Only about 20 elements of the Periodic Table contribute significantly to the maintenance of life on Earth, though up to 60 have been detected in living tissues, and all the elements found in the surrounding environment must be present in trace amounts in living tissues. In cells the elements exist as compounds and complexes of various kinds. About one-third of the enzymes known in biochemistry are active only in the presence of metal ions. Of the metals discussed in this review zinc is biologically the most important[161].

Pelagic organisms can store TM from their surroundings and adapt to changes in their natural concentrations in water and in their nutrients. Geometric mean concentrations of Hg, Cd, and Zn in different types of marine organism (excluding data from heavily polluted regions[60]) are listed in Table 5 together with their ranges (including pollution effects).[162] The TM content is not the same in different tissues of the organism: in heavily contaminated environments the concentration of TM is highest in liver and kidney tissues[60]. The take-up of TM is usually proportional to the growth and final size of the living organism.[163,164] In general the TM content is controlled by many factors which are difficult to consider jointly. For example, in fishes the concentration of mercury depends on the availability of food and on its mercury content, on the chemical form and concentration of mercury in the dissolved state, on the type of fish and its position in the food chain, and on the age, sex, and size of the fish. It is important to note that the concentrations of TM in fishes recently netted from one particular region and in fishes netted several decades ago (museum specimens) are almost identical[165]. However, concentrations can fluctuate, seasonally as well as annually[166]; a marked decrease in TM concentration has been noted[167] in starving invertebrates. The dynamics of the biological accessibility of mercury in a small estuary are discussed in Ref. 168.

Table 5. Geometric mean concentrations of mercury, cadmium, and zinc in different groups of marine organisms (over the whole organism, except shell molluscs)[60] and concentration ranges[162] in μg g^{-1} of dry weight.

Dry weight, %	Organism	Hg		Cd		Zn	
		Ref.60	Ref.162	Ref.60	Ref.162	Ref.60	Ref.162
~20	Marine algae (all types)	0.15	0,002—0.008	0.5	0.86—2.41	90	11—666
—	Phytoplankton	0.17	—	2	1.5—1.8	38	7.1—136
~11	Zooplankton (Copepoda)	0.1	—	4	1.2—2.6	113	9.9—625
~5	Tunicata (mainly Ascidia)	0.1	—	1	0.02—0.2*	200	10—14*
~20	Bivalve molluscs	0.4	—	2	—	100	—
~20	Oysters	0.4	—	10	—	1700	—
~20	Gastropoda	0.2	0.03—0.33	6	0.25—46	200	2.6—2354
22—54	Echinoderms	0.3	—	2	—	100	—
~30	Crustaceans (Decapoda)	0.4	<0.02—0.44	1	0.1—5	80	20—121
3—19	Coelenterata	0.1	—	1	—	50	—
~25	Cephalopoda	0.3	—	5		250	—
~25	Fishes	0.4	0.026—2.6	0.2	0.01—200	80	0.5—396

* per 1 g of live weight.

Organisms can accumulate relatively large amounts of metal: for example, in fishes the concentration factor (from water to fish) is 2.9×10^3 and 10.6×10^3 for open and coastal sea waters respectively[169]. Species such as swordfish and tunny, being at the apex of the food chain, usually contain large concentrations of TM (for example, mercury[170]), which are normal for these species. Some organisms (such as large sea-weeds and mussels) can accumulate TM selectively in some tissues only, and have therefore been selected as indicators of the level of contamination of the water medium.[171] The metal content of organisms can reflect fairly accurately the concentration in the water: for example, mussels have been used to determine mercury in water to a sensitivity of 0.005—0.010 μg $litre^{-1}$.[172]

Metals are absorbed by the tissues of living organisms as a result of adsorption on body surfaces, breathing organs, and alimentary canals (in the case of metals ingested with the food); adsorption is followed by diffusion through cell membranes and combination with organic ligands contained in the cells.[60] The extent of absorption depends on many factors: the chemical and physical forms of the metals, their concentration, the temperature, the presence of various organic or inorganic compounds, the state of the body surface of the organism, etc. For example, organic mercury is absorbed much more easily than inorganic mercury by fishes, crustaceans, and molluscs because of its solubility in the mucilaginous surface layer of their bodies and gills, which assists its penetration through the cell membranes[60,173]. The rate of absorption of $MeHg^+$ by fishes increases (but not in direct proportion) with concentration and temperature, is independent of the presence of organic compounds (for biochemical oxygen demand values of 8—800 mg $litre^{-1}$), and is a maximum for a Cl^- concentration of ~200 mg $litre^{-1}$.[96] The influence of natural factors on the absorption of mercury and cadmium by mussels is discussed in Refs. 174 and 175. However, great care is needed in predicting *in situ* absorption of metals by marine fauna from laboratory data[173].

After the metal has been absorbed by the organism its distribution in the various tissues can vary markedly with time. Thus, a trout exposed for one day to a solution of MeHgCl containing 10.7 μg Hg $litre^{-1}$ was found to contain ~10 times more methylmercury in its gills than in its other organs, the concentration of MeHgCl being lowest in the brain and in the skeletal muscles. However, the relative amounts changed with time, and after 6 weeks the MeHgCl level of the fish was highest in the brain, skeletal muscles, and gonads[176]. On the other hand the absorption of Cd^{2+} from sea water involves a time lag, but is then linearly related to time and to the concentration of Cd^{2+} (if not too high). The maximum concentration factor is 165 at a concentration of 0.7 μg Cd ml^{-1}. However, the complexes of cadmium with EDTA, humic and alginic acids, and even pectin are absorbed without time lag, and both the rate of accumulation and the final concentration in the tissues increase by a factor of two in the series kidneys ≫ viscera >gills ≫mantle >muscle. Cadmium is excreted 18 times more slowly than it is absorbed (mainly through the kidneys).[176]

The tendency to accumulate different chemical forms of the metals in different tissues has been demonstrated in the case of mercury. Hg^{2+} accumulates mainly in the kidneys, and its concentration in the brain tends to be low. Inhaled mercury vapour enters the blood (in small amounts) as Hg^0, which rapidly diffuses through the hematoencephalitic barrier and is oxidised to Hg^{2+} in the brain. Over 90% of the mercury in blood is found in the erythrocytes, combined with haemoglobin, the remainder being combined with proteins in the plasma. Most of the mercury found in the bile is combined with di- and tri-peptides containing cysteine. On the whole, the distribution of mercury after inhalation of mercury vapour or ingestion of phenylmercury or mercuric diuretics is similar (except for the brain) to the distribution of Hg^{2+}, because of the rapid biotransformation of these forms of mercury into Hg^{2+}. On the other hand in $MeHg^+$ and its alkyl derivatives the Hg–C bond is relatively stable in biological systems, and

therefore these compounds show a different distribution and different biological effects. The high lipid solubility of $MeHg^+$ allows it to pass through the hematoencephalitic barrier and to accumulate in the brain, where it produces irreversible poisoning of the central nervous system.[178] It has been shown that $MeHg^+$ can catalyse the hydration and hydrolysis of vinyl ether bonds in plasmogens (the main constituents of the phospholipids in the cell membrane).[179]

The relative toxicity of these metals towards many forms of marine and estuary life decreases in the sequence[60,180] Hg ≫ Cd > Zn, and the mercury compounds lie in the sequence[181] $RHg^+ > ArHg^+ > Hg^{2+}$. However, these sequences are arbitrary, since the toxicity of the metals depends on their chemical and physical forms, on the dose, on the path by which the metal enters the organism, etc.[180,181] For example, the toxicity is proportional to the concentration of free Cd^{2+} ions in water[182], and decreases in the presence of factors which tend to lower this concentration by changes in form or by complex formation (increased water hardness[183] and salinity[182], presence of organic[182] and humus substances[86]). In general, chelate formation lowers the toxicity of the metals[182], which can be correlated with parameters defining the "hardness" or "softness" of the metals[184]. Surprisingly, $MeHg^+$ and Cd^{2+} inhibit the regeneration of tail-fins in fish, but the effect disappears when these forms are mixed with Hg^{2+}.[185] A toxicological comparison of the effect of Cd, Hg, and Cu on natural and on culture populations of Copepoda has been reported[186]. The toxicology of mercury compounds has been studied in great detail, and widely reported, including biological effects[178,181,187].

Direct electron microscopic evidence has been obtained that oysters can store Cu and Zn in the form of different compounds within bubbles surrounded by membranes in the amebocytes which are present in all the soft tissues, and that these metals are combined with S and P respectively. It is suggested that this mechanism of storage and de-toxification of TM in biological systems may be wide-spread. However, there are important differences between the different metals and the different organisms. Whereas Cu and Zn are stored in amebocytes, and they accumulate mainly in the gills and in the mantle, Fe and Pb are found in bubbles of epithelium cells of the kidneys[188], and Cd becomes concentrated in the kidneys and viscera[177].

The action of many enzymes requires Zn and Cu in the ternary and quaternary protein structures. However, if these enzymes are exposed to excessive concentrations of the functional metals, or to other trace metals able to compete with them (like Hg and Cd), their normal functions may be impaired. This effect may be due to conformational changes, as a result of which the substrate molecules are unable for a long time to "adapt" themselves to the reactive centres of the enzymes. On the other hand, some toxic metals (including mercury) are able to split various enzymes into their regulating and catalytic sub-units, so that the normal regulatory function is lost. Therefore in order to ensure normal cell operation the excess of functional metals (or the toxic metals) must be removed from the biological sphere of action. This is accompanied by the formation of metal thionein (MT), which can combine with TM and biologically deactivate them.[189]

Metal thionein is the principal means of storing Zn and Cu in the liver and kidneys, where it is found in the cell walls of tissues, and it probably contributes to the control of metal adsorption in the mucous lining of the intestine. It is a protein with a MW of 10000–12000, containing an unusually high proportion of cystein (~30% of the total amino-acid residues). The presence of a large number of thiol groups gives the MT a high affinity for metals: 2–3 cystein residues are available to combine with each metal atom for a metal content of 7–10%.[190,191] In living organisms MT is always saturated with metals, and it contains Zn in approximately one-half of the reactive centres. Production of MT can be stimulated by adding Zn and Cu, and also Hg, Cd, and Ag.[190]

One of the modern theories of de-toxification is based on these properties of MT: it states that Hg and Cd are free from toxic effects as long as their concentration is insufficient to exceed the combining power of MT. Hence, when Hg and Cd are ingested into the organism they initially displace from the MT the Zn and Cu (which are much less strongly bound) and transfer them to high-MW proteins (metal-enzymes). Since the displaced metals are naturally occurring components of many of the proteins, they are relatively non-toxic. Only when the concentration of Hg and Cd exceeds the combining power of the MT are these metals transferred to the metal-enzymes, where they begin to display their toxic properties within the cell. However, this transfer depends also on the relative rates of supply of Hg (or Cd) and of MT synthesis (stimulated by the trace metal). Therefore it is suggested[191] that the critical factor determining the survival of the organism is not the concentration of Hg or Cd in the tissues (which can be quite high) but whether the trace metals are located in the MT or in the metal-enzymes.

As was stated above, some species of predatory salt-water fish may contain relatively large amounts of mercury (in some cases >2 mg g^{-1}) without any harm to themselves[170]. This was inexplicable until it was realised that in these cases the mercury is always accompanied by selenium in a 1 : 1 molar ratio (or by an excess of selenium): somehow, the selenium appears to moderate the toxicity of the mercury. It was recently shown that the selenium-containing enzyme glycine-reductase is, in effect, a selenium cysteine, and the de-toxification of mercury by selenium was ascribed to combination of the mercury with selenium-containing peptides and proteins (as in the case of MT). This hypothesis is confirmed by the observation (from PMR spectra[192]) that the affinity towards $MeHg^+$ of the various groups decreases along the series SeH > SH ≫ Se–Se > NH_2 > S–S, SeMe, SMe. In the case of Cd^{2+} the detoxification effect of selenium and the distribution in different tissues were shown[193] to be similar to those of Hg^{2+} but different from those of $MeHg^+$.

At different concentration levels, Zn and Cd in tissues may compete for combination with proteins. Thus, in liver and kidney cytoplasms the inflow of Cd can combine with high-molecular proteins until the combining power of the MT is exceeded if these proteins are not already saturated with Zn. If they are, the excess of Zn and the Cd are taken up by the MT.[189] Even in poisoned molluscs the Zn, Cd, and Cu are combined with low-molecular proteins if the concentration factor is high but not if the concentration factor is low.[194] In water organisms Cd may be found also in the free state[195]. The degree to which Hg is combined with low-molecular proteins can differ in different organs (as was found in oysters)[196].

In spite of the important role of TM in the life processes of various organisms, very little was known until recently of their chemical behaviour in metabolism, their toxicology, and their bio-transformations. The earliest systematic studies concerned their interaction with sulphur-containing amino-acids. It was shown that all the ligand atoms of these amino-acids (sulphur, nitrogen, and oxygen) can combine with the metals, though the type of bond formed depends on the nature of the metal (even for metals from the same sub-group). In aqueous solutions the resulting compounds and complexes are very labile, and the interaction of a given metal ion with the ligand atoms is a function of pH. Therefore a given metal may be bound to different ligands in the crystalline and in the dissolved state. The same is true of the complexes formed with homologous amino-acids, due to differences in packing of the crystal lattice and to differences in conformational and configurational stability.

This effect is easily demonstrated by considering the interaction of M^{2+} with S-methylcysteine (mcyst) and methionine (met). Whereas in an acid solution Zn^{2+} and Cd^{2+} do not react, and Hg^{2+} forms 1 : 2 complexes with an Hg–S bond, in an alkaline solution the M^{2+} ions form chelates of 1 : 2 composition with M–N,O bonds, and in the case of mercury and mcyst with Hg–S,N bonds (according to the PMR spectra). Hence, in the case of mercury complexes in alkaline solutions the strength of individual bonds is less important than the very high stability of the 5-membered Hg–N,O ring as compared with the 6-membered Hg–S,N ring.[197] On the other hand, in the crystalline state the Zn and Cd in 1 : 2 complexes are combined with N and O atoms[198–200], but the Hg in the complexes with mcyst and met is combined with S[201] and with S and O[202] respectively. However, Cd forms 1 : 1 complexes with penicillamine (pen) containing Cd–S,N,O[203] and Cd–S,O[202] bonds, whereas mercury forms only Hg–S bonds[202] (according to X-ray diffraction analysis). In the complexes of Zn^{2+} and Cd^{2+} with histidine (1 : 2 composition) the metals are bound to N (both amino and imidazole) and to O.[204] Measurements of K have shown that the complex-forming power of M^{2+} towards five octadentate ligands containing sulphur and nitrogen atoms decreases in the series Hg > Zn > Cd > Mg > Ca.[205]

The change in the bonding centre with pH (due to competing reactions) has been studied most thoroughly for the $MeHg^+$ complexes of 1 : 1 composition. With simple amino-acids of the glycine type and at low pH the $MeHg^+$ is attached to the carboxylic acid group, and at high pH it is attached to the amino group[23]. With sulphur-containing amino-acids (for example, met) at pH 2 the $MeHg^+$ ion is combined with the thioether group, but as the pH is increased it begins to "float" along the met molecule and appears to form complexes with the carboxylic acid group (though this has not been proved), and at pH 8–9 it forms complexes with the amino group. As the pH is increased still further the complex begins to dissociate, and at pH 13.5 it is fully decomposed[206]. Bonding with cyst and met has been studied in a similar way[23], and the K values of the corresponding complexes have been determined. On the whole, the apparent stability of the complexes of methylmercury with various ligands depends on pH, and at pH 7–9 it decreases in the sequence thiol > amino > OH^- > carboxylic acid > thioether ligand.[206] The way in which $MeHg^+$ is combined in biologically important compounds is discussed in more detail in Ref. 23.

$MeHg^+$ and $PhHg^+$ have been shown[207] to form 1 : 1 complexes with ligands which coordinate through SNO and SSO (pen, cyst, 2,3-dimercaptopropan-1-ol), and 2 : 1 complexes when the ligands are in excess, with Hg–S, Hg–S,N, and Hg–S,S bonds, whereas with SO and NO ligands (N-acetylcysteine, glycine) only 1 : 1 complexes with Hg–S and Hg–N bonds respectively are formed. The K values for these complexes decrease in the series MeHgS > PhHgN ≳ PhHgS > MeHgN ≫ PhHgO, MeHgO and S > N > O (according to i.r. and PMR spectral data, and potentiometric titrations). The latter method also showed the formation of $MeHgL_2^-$ complexes[31] with simple amino-acids, but chelation in these compounds is still uncertain. The 1 : 1 compounds of $PhHg^+$ with cyst and pen are not very stable, and they undergo spontaneous symmetrisation[208]. Lastly, X-ray structural analysis has shown that Hg–S and Hg–S,N bonds are present in MeHg·pen and $(MeHg)_2$.pen complexes[209], Hg–S bonds in the MeHg.cyst complex[210], and Hg–N bonds in the MeHg.met complex[211], the mercury being also weakly coordinated to oxygen in the latter two complexes.

As in the amino-acids, the metal combination centres in peptides depend on pH. Thus, Zn^{2+} and Cd^{2+} in leucylglycine complexes of 1 : 1 composition at pH < 5 are combined with the carboxylic acid group of the glycine residue to form linear structures, whereas at pH > 5 they are combined with the amino and carbonyl groups of the leucine (according to the ^1H and ^{13}C NMR spectra)[212]. Under similar conditions di-, tri-. and pentapeptides form $[Zn_2L_2]^{2+}$ complexes whose K values have been determined by potentiometric titration[213]. In crystalline compounds, on the other hand, Cd and Zn combine with peptides through N (amino) and O (carboxylate and peptide) to give chelate compounds as a rule[199,204]. In the 2 : 1 complexes of $MeHg^+$ with glutathione at pH < 4 both cations are combined with thiol groups, but at pH 4–8 one of the cations is transferred to the amino group and at pH > 10 it dissociates to MeHgOH.[23]

However, the reactions of the metal ions with proteins differ from those with amino-acids and peptides, because in proteins the α-NH_2 and α-COOH groups of long polypeptide chains are separated by the covalent bonds of several residues. This interaction is affected also by the conformation of the peptide chain, which can block a potential attachment point while a remote side chain is in the correct position for the formation of a chelate ring. An example is provided by the metal-enzymes and metal-proteins, in which the strong interaction between the metal and the protein part plays a decisive and biologically specific role[204,214]. Depending on the type of protein, a given metal ion can fulfil various functions, determined by the limitations imposed by the protein environment. Hence the biologic specificity of the metal function probably has a stereochemical origin[161,204]. Information on the complexes of TM with proteins in the crystalline and the dissolved state is given in Ref. 215 with a statement of the amino-acid residue combined with the metal.

The chemical form of the metals undergoes substantial changes during absorption, transport, and storage in biological tissues and liquids. At physiological pH values they are usually combined with peptides, proteins, and other ligands, but in the acid regions of the digestive tract they can exist in uncomplexed forms[190]. The reactive centres of proteins and enzymes for the attachment of all forms of mercury[187] (and probably also of cadmium[216]) are almost exclusively thiol groups.

It has been suggested that the whole of the $MeHg^+$ present in tissues is combined with cystein-containing peptides and proteins, containing thiol groups. However, in spite of the high thermodynamic stability of these compounds, they can easily exchange with other thiol groups as a result of bimolecular nucleophilic substitution by the reaction $MeHgSR + R'S^- \rightleftharpoons MeHgSR' + RS^-$. This fast exchange, which takes place at physiological pH values, is accompanied by redistribution of the $MeHg^+$ between these groups, which makes the identification of the initial compounds extremely difficult. Conversely, in the stomach (at pH 1.5–2.5 and high concentrations of Cl^-) exchange occurs by the reaction $MeHgSR + H^+ \rightleftharpoons MeHg^+ + RSH$, and most of the methylmercury is in the form of fat-soluble MeHgCl.[178,217]

Metal ions are necessary also for the biologic functions of nucleic acids, and they play an important part in many metabolic processes involving nucleotides as monomers. However, Hg^{2+} compounds can denature native DNA, sometimes reversibly, and $MeHg^+$ causes chromosome disturbance and therefore acts as a mutagen[181]. Furthermore, mercurated nucleotides hinder the synthesis of RNA in the nucleus (by 30–40%).[218] Hence, the interaction of Hg^{2+} (and especially of $MeHg^+$) with the components of nucleic acids has been studied in detail, whereas data for other metals tend to be fragmentary. In general metal ions can be combined with various reactive centres of purine and pyrimidine bases in nucleotides and nucleosides, with formation of both mono- and poly-nuclear complexes and compounds, depending on the base, the pH,

the metal, and the concentration. Thus, in solid complexes of Hg^{2+}, Cd^{2+}, and Zn^{2+} with ATP the metals are combined with N(7) of adenine and with phosphate[219], and Cd^{2+} with uridine (C=O(4)) and ribose, whereas with thymine only the deoxyribose group is involved (according to i.r. spectra).[220] The stereoselectivity of the attachment of the metals to the nucleic acid components is discussed in Ref. 221.

Hg^{2+} and $MeHg^+$ are usually attached to N(1) in purine nucleosides and to N(3) in pyrimidine nucleosides. With bases, $MeHg^+$ forms its strongest bonds with uracil and thymine. It is thought[181,222] that the denaturing of native DNA by Hg^{2+} and $MeHg^+$ involves initially the deprotonation of N(3) in thymidine, and then of N(1) in guanosine (according to Raman spectra). $MeHg^+$ may additionally be combined with ribose and (very weakly) with phosphate[181].

Relatively little is known about the action of TM on marine flora. The highest concentrations of individual TM (Hg, Cd, Zn, As, etc.) which are harmless to marine fauna are also non-toxic to fresh-water phytoplankton, but mixtures are extremely toxic, and can inhibit ~70% of the primary productivity. Cadmium can have both synergic (with Cu and Zn) and antagonistic effects (with Se).[223] At a cadmium concentration of 2 μg $litre^{-1}$ the growth rate of diatomaceous algae decreases by an order of magnitude[224], and at 5–10 μg $litre^{-1}$ the microbial colonisation and decomposition of foliated material is inhibited[225]. However, only a few of the 99 species of phytoplankton examined were found to absorb Hg^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+} *in situ*, and these account for only a very small part of the bio-mass.[226] The effect of TM on the Laminariaceae is described in Ref. 227.

In an experiment lasting 72 days, carried out in a reservoir of 1300 m^3 capacity covered with a plastic sheet, the productivity of phytoplankton was found[228] to decrease after 12 days in the presence of 5 μg $litre^{-1}$ of mercury, and zooplankton could not be detected after 34 days. The concentration of dissolved mercury was less than 50% of the total mercury content, which fell by 3% per day. At the end of the experiment >90% of the mercury was found in the bottom sludge[228].

VII. BIOLOGICAL CONVERSION OF THE FORMS

Among the metals under discussion, only mercury can exist in nature in different states of oxidation and form stable mercury-organic compounds. Therefore, biological conversion of the forms (especially methylation and demethylation) has been studied mainly with mercury derivatives. In biological systems three coenzymes can act as methylating agents: S-adenosylmethionine, N^5-methyltetrahydrofolates ($Me-N^5$), and vitamin B_{12} derivatives (methyl corrinoids). All these substances can transfer a methyl group as the Me^+ cation, but only the methyl corrinoids can generate it also in the form of the Me^- anion and the Me· radical, which enables them to methylate Hg^{2+} salts and Hg^0 respectively. Methyl cobalamin $Me-B_{12}$ (one of the methyl corrinoids) is found in microorganisms and in warm-blooded animals: it produces $MeHg^+$ and Me_2Hg by enzymic and non-enzymic paths in relative amounts depending on the concentration of mercury.

The mechanism of non-enzymic methylation of $Hg(OAc)_2$ by methyl cobalamin in aqueous solution is believed to involve heterolytic breaking of the Co–Me bond without change in valency of the Co^{3+}, followed by transfer of Me^- to the Hg to give $MeHg^+$ and aquocobalamin as the end-products. Being highly electrophilic, Hg^{2+} can also coordinate with the $Me-B_{12}$ base through 5,6-dimethylbenzimidazole (DMBI) to give a mixture of $Me-B_{12}$ complexes both with and without breaking of the Co–DMBI bond. The first complex reacts with Hg^{2+} at least 1000 times faster than the second, because of the greater electron density in the Co–C bond resulting from coordination to the DMBI. Me_2Hg is formed in a similar way, but only from $MeHg^+$, and at a rate 6000 times smaller[229].

However, the demethylation of $Me-B_{12}$ induced by Hg^{2+} in chloride or acetate solutions was found[230] to occur in a single step, without breaking of the Co–DMBI bond, whereas Hg^{2+} in aqueous solutions can break this bond reversibly as a result of complex formation with DMBI by the reaction $Me-B_{12}+Hg^{2+} \rightleftharpoons Me-B_{12}-Hg^{2+}$. In the latter case the methylation kinetics are complex, and depend on the concentration of Hg^{2+}.

The reaction rate is very sensitive to the degree of dissociation of the mercury salts, and for the synthesis of $MeHg^+$ it decreases in the sequence[231] $OAc^- > Cl^- > Br^-$ (the rate constant of the reaction for mercuric acetate and cyanide respectively being 260×10^{-4} and $< 0.01 \times 10^{-4}$ s^{-1}).[229] In the case of Me_2Hg the corresponding series is[187,229] $Cl^- > OH^-$. This reaction is inhibited by phosphates and thiols. Non-enzymic electrophilic methylation of mercury is found in aerobic organisms, which contain methyl corrinoids as metabolic intermediates.

The free radical mechanism for the methylation of mercury by $Me-B_{12}$ has not been investigated, but in the case of other metals and metalloids (for example, for Cr^{2+}) it has been shown to involve homolytic breaking by these elements of the Co–C bond of methyl cobalamin to give Co^{2+}–cobalamin and the corresponding methyl derivative. The reaction takes place only in the presence of oxygen (which is needed to generate the radicals[229]).

It has been suggested that the mechanism of the methylation of elements by $Me-B_{12}$ depends on the standard reduction potential E^0 of the element. For $E^0 > 0.8$ V an electrophilic mechanism is predicted for the most highly oxidised members of redox couples (for example, Pb^{4+}/Pb^{2+}, Pd^{2+}/Pd^0, and Hg^{2+}/Hg^0), and for $E^0 < 0.154$ V a radical mechanism for the least oxidised members of redox couples (for example, Sn^{4+}/Sn^{2+} and Cr^{3+}/Cr^{2+}). The range $0.154 \text{ V} < E^0 < 0.8$ V includes the elements for which both members of the couple can be methylated. It is important to note that for some elements (e.g. Se) the methylation mechanism can vary with pH.[229]

Methyl corrinoids also take part in the enzymic synthesis of $MeHg^+$ in the presence of the enzyme methionine synthetase, found in various aerobic and anaerobic micro-organisms and in the liver of mammals, which slowly catalyses the reaction. The suggested mechanism includes the transfer of Me^- from the $Me-B_{12}$ co-enzyme to the enzyme in the presence of catalytically active amounts of S-adenosylmethionine. The enzyme–co-enzyme complex is re-methylated by Me^+ provided by $Me-N^5$. This complex can nucleophilically methylate Hg^{2+}, forming $MeHg^+$ and an aquocobalamin–enzyme complex which can be reconverted into the original complex by the action of flavin adenine dinucleotide (which reduces Co^{3+} to Co^+), followed by methylation of the complex by $Me-N^5$. In the presence of cysteine $MeHg^+$ forms methylmercury cysteine, which can give MeHgSMe in the presence of an excess of Me^+.[187]

The microbiological methylation of Hg^{2+} was first demonstrated *in vitro* with lake sludges[232], but it was subsequently found *in vivo* in marine[233] and river deposits[234]. With $PhHg^+$ the process occurs even more readily, and it seems likely that any form of mercury is converted (at least, partly) into $MeHg^+$ in a water environment. Bio-methylation by bacteria and molds is possible under both aerobic and anaerobic conditions[233,235,236]: in this case the main reaction product is $MeHg^+$ under aerobic conditions, and under anaerobic conditions (in the absence of S^{2-}) the main product is Me_2Hg[235] and methylation proceeds more easily[233]. The rate of the reaction is proportional to the metabolic activity of the microorganisms, to the total concentration of Hg^{2+} ions and their

availability, and to temperature[98,234-236]. Methylation is assisted by the presence of organic substances[96,233,234]; it depends on the salinity, and the process is most effective at a Cl^- concentration of ~200 mg litre^{-1}.[96] The optimum pH value for the synthesis of $MeHg^+$ is 4.5.[237] At pH 7 the rate of methylation is highest[96], and the main product is $MeHg^+$, but small amounts of Me_2Hg are also formed[236]. Early studies of methylation are reviewed in Refs.235 and 238.

We should note that bio-methylation of mercury has not been observed in plants and soils[235]: in these systems $MeHg^+$ can be formed by a non-biological path. The methylating factor can be extracted by alkali, and is decomposed by radiation. It is thought to consist of fulvic rather than humic acids, since solutions of the latter do not methylate mercury[239].

Bio-methylation under natural conditions is always accompanied by bio-demethylation to inorganic mercury, leading to an equilibrium concentration of $MeHg^+$ (or, more exactly, an equilibrium ratio of $MeHg^+$ to total mercury). This conclusion was reached from studies of river[240] and marine[241] sludges *in vitro*. Bio-degradation is probably faster under aerobic than under anaerobic conditions[233], though similar rates have been reported[240].

Experiments with isotopically labelled mercury have shown that in river sludges the *in vitro* mineralisation of $MeHg^+$ and methylation of Hg^{2+} depends on the type of deposit, and that the two processes are favoured by low and by high concentrations of organic matter respectively. Equilibrium concentrations of $MeHg^+$ of 0.2 and 12% were obtained, the equilibration times being 3 and 6 months respectively[67].

Many organic derivatives of mercury are decomposed by bacteria to Hg^0.[187,238] The same end product can be obtained by reducing Hg^{2+} with an enzyme found in various bacteria, which requires reduced nicotinamide adenine dinucleotide as a co-enzyme (NADH):[237]

$$Hg^{2+} + NADH + H^+ \rightleftharpoons Hg^0 + 2H^+ + NAD^+ \ .$$

Aerobic micro-organisms bring Hg^{2+} into solution from HgS as a result of the oxidation of sulphide to sulphate ions.

Bacteria and their metabolites play an important role in the transport of Zn^{2+} and Cd^{2+} from sea water to the bottom deposits. Because of the large quantities of H_2S produced by bacteria it is assumed that the metals are precipitated as MS or coprecipitated with FeS, since only ~20% of the deposited Zn^{2+} and a negligible proportion of the Cd^{2+} are found within the bacterial cells.[242]

Very little work has been done on the biological conversions of mercury compounds in living marine organisms. Thus, $HgCl_2$ introduced in various ways into a rainbow trout is not methylated[243], whereas MeHgCl is partly decomposed after being absorbed by the trout[176] (*in vivo* experiments). However, these conclusions may be erroneous because of the inadequate experimental conditions. Published data on the ratio of $MeHg^+$ to total mercury in fishes tend to be inconsistent[244].

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We may conclude from this review that the penetration of chemical and physicochemical concepts and methods into our understanding of the role of the chemical forms of mercury, cadmium, and zinc in natural water environments is still inadequate. However, owing to the increasing impact of chemicals of anthropogenic origin on the ecological equilibrium, a more active participation in these studies from chemists of different specialisations is highly desirable.

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The Use of Taft Relations for the Correlation of the Properties of Organosilicon Compounds. The Role of Substituent Effects

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Data for the correlations between the properties of organosilicon compounds on the basis of Taft equations are surveyed for the first time. The results for 140 relations involving reactivities, capacities for complex formation, and spectroscopic characteristics are examined. The specific features of the influence of individual effects of substituents at the silicon atom and the ability of the silicon atom and silicon-containing groups to transmit effects are discussed.
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I. INTRODUCTION

The only common and practically feasible approach to a quantitative description of the relations between the properties of organic compounds and their structure available at present is the Hammett–Taft theory. The fundamental postulate of the theory, based on the thermodynamic principle of linear free energy relations (LFE), presupposes that, to a first approximation, the influence of individual effects of substituents (inductive, resonance, etc.) on the given property of the molecule is additive[1–3].

Since the LFE principle is general, analogous relations are observed also for compounds where the indicator centre does not consist of carbon but of other elements. Among these, organic derivatives of phosphorus and silicon have been most widely investigated. An extremely significant feature of the electronic structures of these (and other) elements of the Third Period, responsible for their difference from carbon, is the possibility of p_π–d_π interaction via the d orbitals energetically available for combining with other reactants, which have an excess p- or π-electron density†. Quantum-chemical calculations on the p_π–d_π interaction predicted its intensification with increase of the positive charge of the atom of the Third Period on σ-bonding to electronegative substituents[6]. A pronounced pair interaction between the inductive and resonance effects of the substituents was therefore to be expected in this instance. Nevertheless, in organic derivatives of phosphorus, for which experimental data concerning relations of the Hammett–Taft type have already been reliably surveyed, systematic deviations from the additivity have not been observed[7].

In this review the first attempt is made to survey the available literature data concerning the application of various modifications of the Taft equation to aliphatic organosilicon compounds. As regards the structure-property correlations for aryl derivatives of silicon, we shall only mention that the Hammett equation in its traditional form is applicable to almost all cases.

†It is noteworthy that the p_π–d_π interaction constitutes the most widely accepted hypothesis used to account for a number of anomalies in the properties of elements with vacant d orbitals. Other views have also been described[4,5].

II. EXPERIMENTAL RESULTS

The available data on the structure–property correlations for organosilicon compounds are presented in Tables 1–3. The following numbering of the equations has been adopted:

$$A_i = A_0 + \rho^* \sum \sigma_i^*; \quad (1)$$

$$A_i = A_0 + \rho^* \sum \sigma_i^* + \delta \sum E_{s_i} \quad (2)$$

where A_i are numerical characteristics of the given property, σ_i^* are the Taft constants of the substituents, E_{s_i} are the steric constants of the substituents, and ρ^* and δ are the corresponding slopes.

The deviations from these equations are noted separately. The following notation is used in Tables 1–3: r and R are the coefficients of pair and multiple correlation respectively, n is the number of compounds the values of A_i for which were used in the correlation (the number of points), and s is the standard error of the correlation. It is also indicated which particular steric constants (E_S, E_S^C, and E_S^0) or non-Taft inductive constants [σ_i and σ(Si)] of the substituents were used in the original studies. In those cases where an independent and non-contradictory interpretation of the results exists for similar reaction series based on the same property, Tables 1–3 list only the data based on more extensive experimental results (the corresponding literature references are underlined). Certain relations (designated by an asterisk opposite the reference) were found by ourselves from literature data either for the first time or from an equation other than that given in the original communication.

Apart from the reports listed in Tables 1–3, there have been a number of publications in which the dependence of the given property on the constants of the substituents at the silicon atom was illustrated only in graphical terms. The relations between the logarithms of the rate constants and the Taft constants for the acid solvolysis of dimethylorganylsilanes[93], the cleavage of the Si–O bond in Me_3SiOR

Table 1. Correlations of reactivities.

No.	Reaction	Quantity correlated	No. of Eqn.	A_0	ρ^*	δ	r(R)	n	Remarks	Refs.
1	$R_3SiH + H_2O \xrightarrow{EtOH,\ HCl,\ 35°} R_3SiOH + H_2$	$\lg k$	(1)	−2.72	0.77	—	0.96	14	s = 0.09, R = n-alkyl and substituted alkyl	8
2	ditto	$\lg k + 3$	(2) (E_s^c)	0.51	0.0	0.32	0.99	7	R = n-alkyl, isoalkyl, or substituted alkyl	9
3	$R_2SiH_2 + 2H_2O \xrightarrow{EtOH,\ HCl,\ 35°} R_2Si(OH)_2 + 2H_2$	$\lg k_1$	(1)	−1.77	0.77	—	0.97	4	s = 0.06; R = H, n-alkyl, or substituted alkyl	8
4	$R_3SiH + H_2O \xrightarrow{EtOH,\ KOH,\ 0°} R_3SiOH + H_2$	$\lg k_{rel}$	(1)	—	4.42	—	0.99	14	R = n-alkyl or substituted alkyl but not $Ph(CH_2)_n$	10
5	ditto	$\lg k_{rel}$	(2) (E_s^c)	—	1.74	0.39	0.96	11	R = n-alkyl or $Ph(CH_2)_n$ (n = 1,2, or 3)	9
6	$RSiH_3 + 3MeOH \xrightarrow[k_1,\ k_2,\ k_3]{DMF,\ KOH,\ 20°} RSi(OMe)_3 + 3H_2$	$\lg k_1$	(1)	−0.93	1.76	—	0.96	6	R = n-alkyl, isoalkyl, substituted alkyl, or Ph	11
7	ditto	$\lg k_2$	(1)	−0.21	1.40	—	0.92	4	R = n-alkyl, isoalkyl, or substituted alkyl	11
8	»	$\lg k_3$	(1)	−0.94	1.76	—	0.98	5	R = n-alkyl, substituted alkyl, or Ph	11
9	$R_3SiH + O_3 \xrightarrow[-O_2]{CCl_4,\ 20°} R_3SiOH$	$\lg k$	(1)	1.7	−0.70	—	0.99	6	R = n-alkyl or benzyl	12, 13
10	$R_3SiH + Br_2 \xrightarrow[-HBr]{CCl_4,\ 20°} R_3SiBr$	$\lg k$	(1)	4.5	−2.38	—	0.99	5	s = 0.22; R = n-alkyl or substituted alkyl	14*, 15
11	$R_3SiH + Cl_2 \xrightarrow[-HCl]{CCl_4,\ 80°,\ h\nu} R_3SiCl$	$\lg k_{rel}$	(1)	—	−0.11	—	0.99	5	R = Me, Et, Ph, or Cl	16, 17
12	$Me_2RSiH + N_2CHCO_2Et \xrightarrow[-N_2]{90°,\ Cu} Me_2RSiCH_2CO_2Et$	$\lg k$	(2) (E_s^0)	−0.14	−1.25	0.11	0.99	6	R = n-alkyl or isoalkyl	18
13	$R_3SiH + Me_3SiCOPh \xrightarrow{20°} R_3SiCH(Ph)OSiMe_3$	$\lg k_{rel}$	(2) (E_s)	—	2.13	0.87	0.99	4	R = H, Ph, $PhCH_2$, or cyclo-C_6H_{11}	19
14	$R_3SiH + CH{\equiv}CC_4H_9 \xrightarrow[H_2PtCl_6,\ 20°]{THF,} R_3SiC_6H_{11}$	$\lg k_{rel}$	(2) (E_s^0)	0.39	0.0	0.41	0.94	5	s = 0.12; R = n-alkyl or isoalkyl	20
15	$2Me_2RSiH + MeP(O)(OH)_2 \xrightarrow[-2H_2]{C_5H_5N,\ 65°} MeP(O)(OSiRMe_2)_2$	$\lg k$	*	−1.73	5.49	0.27	0.99	8	h = 0.27, s = 0.02; R = n-alkyl or isoalkyl	21
16	$RSi(OCH_2CH_2)_3N$, hydrolysis (20°)	$\lg k$	(1)	−1.54	4.76	—	—	5	R = H, Vin, n-alkyl, or isoalkyl	22
17	$ROSi(OCH_2CH_2)_3N$, hydrolysis (20°)	$\lg k$	(1)	−4.81	2.60	—	—	5	R = n-alkyl or isoalkyl	22
18	ditto (HCl, 25°)	$\lg k$	(1)	**	−1.26	—	0.99	4	s = 0.005; R = n-alkyl or isoalkyl	23
19	$Me_3SiOR + MeOH \xrightarrow[-ROH]{EtNH_2,\ 20°} Me_3SiOMe$	$\lg k_{rel}$	(2) (E_s)	−0.07	4.64	0.62	0.96	7	R = n-alkyl, isoalkyl, or substituted alkyl	24
20	$Me_3SiOCOR + HOCH_2Ph \xrightleftharpoons{CCl_4,\ 20°} Me_3SiOCH_2Ph + RCOOH$	$\lg K$	(1)	**	−0.57	—	0.99	13	R = n-alkyl, isoalkyl, substituted alkyl, or Ph	25
21	$n\,(MeRSiO)_3 \xrightarrow[NaOH]{100°,} (MeRSiO)_{3n}$ (polymerisation)	$\lg k_{rel}$	(1)	—	0.21	—	0.99	4	R = Ph or substituted aryl	26
22	$(Me_2SiO)_2MeRSiO \xrightarrow[DMSO,\ 50°]{KOH,} \text{polymerisation}$	$\lg k_{rel}$	(1)	—	0.43	—	0.93	5	R = n-alkyl, Vin, Ph, or chlorophenyl	27, 28, 29
23	$MeRSi(-O-SiRMe-CH_2CH_2)_2 \xrightarrow[KOH]{120°,} \text{polymerisation}$	$\lg k_{rel}$	(1)	—	0.06	—	—	4	R = n-alkyl	30
24	$(R_3SiO)_2 + Bu_4NOH \xrightarrow{pyridine\ 25°} HO(R_3SiO)_3NBu_4$	$E^{0,5}$, eV	(1)	−1.0	0.1	—	—	7	R = Me, substituted alkyl, Ph, or Vin	31
25	$2R_3Si(OH)_2 \xrightarrow[Et_3N,\ 25°]{MeOH,} HO(R_2)SiOSi(R_2)OH + H_2O$	$\lg k_{rel}$	(1)	—	4.7	—	—	4	R = Me, substituted alkyl, Ph, or Vin	32
26	ditto (MeOH, HCl, 25°)	$\lg k_{rel}$	(2) (E_s^c)	—	−0.32	1.02	0.93	7	s = 0.20; R = n-alkyl or substituted alkyl	33*
27	$R_3SiCl + H_2O \xrightarrow[-HCl]{acetone,\ -45°} R_3SiOH$	$\lg k$	(2) (E_s^c)	***	0.62	0.61	0.99	5	s = 0.12; R = n-alkyl or substituted alkyl	34
28	$R_3SiCl + HO(Me_2)SiCB_{10}H_{10}CH + Et_3N \xrightarrow[-Et_3N\cdot HCl]{toluene,\ 20°} R_3SiO(Me_2)SiCB_{10}H_{10}CH$	$\lg k$	(2) (E_s^c)	**	1.91	1.35	—	5	R = H, n-alkyl, or substituted alkyl	35
29	$R_3SiCl + Me_3NSiMe_2 \xrightleftharpoons{CCl_4,\ 37°} R_3SiNMe_2 + ClSiMe_2$	$\lg K_{rel}$	(1)	—	0.89	—	0.99	12	R = n-alkyl, isoalkyl, substituted alkyl, Ph, or Vin	36
30	$R_3SiCl + Me_3SiOEt \xrightleftharpoons[\text{hexamethylphosphoramide}]{toluene,\ 20°} R_3SiOEt + Me_3SiCl$	$\lg K_{rel}$	(2) (E_s^0)	—	1.02	0.82	0.98	6	s = 0.03; R = n-alkyl or substituted alkyl	37
31	$R_3SiF + MeO^- \xrightarrow{MeOH,\ 20°,\ MeONa} R_3SiOMe + F^-$	$\lg k_{rel}$	(1)	—	1.44	—	0.99	5	s = 0.07; R = n-alkyl, Ph, or benzyl	38
32	$R_3SiF + Et_4NOH \xrightarrow{pyridine,\ 25°} R_3SiOH + Et_4NF$	$(E_i^{0,5} - E_0^{0,5})/0.059$ eV	(1)	—	1.61	—	0.99	5	R = n-alkyl, benzyl, Ph, or Vin	39
33	$R_3SiNHMe + H_2SiPh_2 \xrightarrow[-H_2]{anisole} R_3SiN(Me)SiPh_2H$	$\lg k$	(1)	**	2.46	—	0.98	9	R = n-alkyl, isoalkyl, substituted alkyl, or Vin	40
34	$R_3SiCB_{10}H_{10}CH + BuOH \xrightarrow[Bu_2O,\ KOH,\ 60°]{} R_3SiOBu + HCB_{10}H_{10}CH$	$\lg k$	(1)	**	0.92	—	0.93	6	R = n-alkyl, substituted alkyl, or alkoxy-group	41
35	$R_3SiCH{=}CH_2 + AcSH \xrightarrow{ethylbenzene\ 40°} R_3SiCH_2CH_2SAc$	$\lg k_{rel}$	(1)	—	−0.5	—	—	7	R = Me or substituted alkyl	42
36	$R_3Si(CH_2)_nSCH{=}CH_2$, hydrolysis (DMF, 20°)	$\lg k$	(1)	−3.89	−2.72	—	0.99	5	s = 0.03; R = Me or Et, n = 1,2, or 3	43

*The equation $\lg k_i = \lg k_0 + \rho^*\sigma^* + \delta E_S^0 + \Delta n_H h$ was used here.
**Data not quoted in the original communication.

Table 2. Correlations of capacities for complex formation in terms of Eqn.(1).

No.	Complex	Method of investigation	Quantity correlated	A_0	ρ^*	r(R)	n	Remarks	Refs.
1	Phenol + R_2O (ether)	i.r.s.	$\Delta\nu$(OH) for phenol, cm^{-1}	263	—90	0.98	9	—	44
2	Phenol + R_3SiOEt	i.r.s.	$\Delta\nu$(OH) for phenol, cm^{-1}	275	—61.3	0.98	12	$s=6$	45
3	Phenol + $(R_3Si)_2O$	i.r.s.	$\Delta\nu$(OH) for phenol, cm^{-1}	162	—43	0.95	22	$s=11$	45
4	Phenol + $RSi(OEt)_3$	i.r.s.	$\Delta\nu$(OH) for phenol, cm^{-1}	237	—25	0.99	5	—	46
5	Phenol + $RSi(OMe)_3$	i.r.s.	$\Delta\nu$(OH) for phenol, cm^{-1}	226	—32	0.96	6	—	46
6	Phenol + $R_nSi(OCH_2C\equiv CH)_{4-n}$	i.r.s.	$\Delta\nu$(OH) for phenol, cm^{-1}	234	—14.5	0.97	6	$s=10$	47
7	Phenol + $ROSi(Me_2)C\equiv CH$	i.r.s.	$\Delta\nu$(OH) for phenol, cm^{-1}	228	—76	0.95	7	$s=6.5$	48
8	Phenol + $R(Me_2)SiOR'$	i.r.s.	$\Delta\nu$(OH) for phenol, cm^{-1}	272	—47	0.97	11	$s=5$	49
9	Phenol + Me_3SiOR	i.r.s.	$\Delta\nu$(OH) for phenol, cm^{-1}	275	—73	—	16	*; $\rho_i^*=-75$	50
10	Phenol + Me_3SiOR	i.r.s.	$\Delta\nu$(OH) for phenol, cm^{-1}	263	—82	0.94	14	$s=12$	50*, 51
11	Phenol + $Me_2ClSiOR$	i.r.s.	$\Delta\nu$(OH) for phenol, cm^{-1}	**	—88	—	7	—	51
12	Phenol + $MeCl_2SiOR$	i.r.s.	$\Delta\nu$(OH) for phenol, cm^{-1}	**	—39.5	—	7	—	51
13	Phenol + $R_3SiOOSiPh_3$	i.r.s.	$\Delta\nu$(OH) for phenol, cm^{-1}	190	—19	0.93	11	$s=5$	52*
14	Phenol + $R_3SiOOCMe_3$	i.r.s.	$\Delta\nu$(OH) for phenol, cm^{-1}	198	—41	—	6	—	53
15	Phenol + $R_3SiOOGePh_3$	i.r.s.	$\Delta\nu$(OH) for phenol, cm^{-1}	219	—33	0.89	7	$s=3$	52*
16	$RSi(OEt)_3 \cdot SnCl_4$	calorimetry	q, kcal mol^{-1}	7.85	—1.03	0.95	4	q = heat of complex formation	54
17	$R_2Si(CH_2)_3$ + tetracyanoethylene (TCE)	u.v.s.	E_{CT}, eV	3.56	2.38	0.99	8	$s=0.015$; E_{CT} = energy of first charge-transfer bands	55
18	Ditto	u.v.s.	I, eV	9.33	2.77	0.99	8	$s=0.02$; I = ionisation potental of donor	55
19	$RSCH_2Si(OCH_2CH_2)_3N$ + TCE	u.v.s.	I, eV	8.26	1.66	0.99	6		56
20	$R_3SiCH_2NMe_2$	potentiometry	pK_a	9.12	—1.76	0.98	7	—	56
21	$R_3SiCH_2NEt_2$	potentiometry	pK_a	8.60	—1.95	0.99	6	—	57
22	R_3SiOH + DMSO	^{1}H NMR	$\Delta\delta$(HO) ****	307.4	65.0	0.99	6	$s=6$	58*
23	R_3COH + DMSO	^{1}H NMR	$\Delta\delta$(HO)	242.1	73.1	0.96	7	$s=15$	58
24	$Me_3SiOR + HCCl_3$	^{1}H NMR	$\Delta\delta$(H) *****	0.35	—0.41	—	8	$\delta=0.26$ ***	59

*The equation $\Delta\nu_i = \Delta\nu_0 + \rho^* \sum \sigma_i^* + \rho_1^* + (\sum \sigma_i^*)^2$ was used.

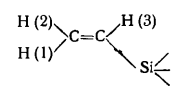
**Data not quoted in the original communication.

***Eqn.(2) was used.

****Relative to trimethylsilane; the values of $\Delta\delta$ are expressed in Hz.

*****Relative to Me_2O.

with the aid of butyl-lithium[94], the solvolysis of bis(trialkylsilyl) sulphides[95], the thermal decomposition of triorganyl(t-butylperoxy)silanes[96], the anionic polymerisation of cyclotetrasiloxanes $(Me_2SiO)_n[Me(CF_3CH_2CH_2)SiO]_{4-n}$, where $n = 0-3$ [97], and the dependence on the Taft constants of the constants for chain transfer by triorganylsilanes in the radical polymerisation of olefins[98], of the relative acidities of alkyl(triorganylsilyl)amines and hexaorganyldisilazanes calculated from the values of $\Delta\nu$(NH) in the infrared spectra of mixtures of the above compounds with a ligand [tetrahydrofuran (THF) and dioxan] [99], of the relative basicities of methyl(triorganylsilyl)amines determined by ^{1}H NMR from the change in the chemical shift $\Delta\delta$ of the proton in chloroform in equilibrium with a mixture of the above compounds[100], of the stretching vibration frequencies of the Si–Ci bond in the infrared spectra of triorganylchlorosilanes[101], of the stretching vibration frequencies $\Delta\nu$(OH) and the corresponding values of $A^{0.5}$ in the infrared spectra of triorganylsilanols[102], of the chemical shifts $\tau(H_3-CSi)$ [but not τ(H–Si)] of methyldiorganylsilanes MeRR'SiH, of the shifts $\tau(-CH_2)$ [but not $\tau(-CH_3)$] of the protons in the ethyl groups of the compounds EtRR'SiH [103], EtRR'SiVin [104] [here and subsequently Vin stands for vinyl – $CH=CH_2$ (Ed.of Translation)], and Et_nSiX_{4-n} (X = halogen) [105], of the chemical shifts of the H(1) protons [but not H(3)] of the vinyl group



in the ^{1}H NMR spectra of all the compounds R_3SiVin [104], of the frequencies ν_m[77] (^{35}Cl) in the NQR spectra of the compounds Me_nSiCl_{4-n} ($n=1-4$), $(EtO)_{4-n}SiCl_n$ ($n=1-4$), and $(MeO)_{4-n}SiCl_n$ ($n=1-3$) [106], and of the dipole moments of vinylorganyldimethoxysilanes[107] were described in this way. There is a relation between the dipole moments of phenyltrialkoxysilanes ($r=0.91$) and the E_S^0 of the alkyls in the alkoxy-groups but not the σ^* of these substituents ($r=0.55$).[108] The dependence of the logarithm of the rate constant for the addition of the trichloromethyl group in chlorobenzene to triorganylvinylsilanes $Me_2RSiVin$ (R = n-, iso-, or t-alkyl) at 80 °C on the steric constants of the substituents R has been demonstrated graphically[109].

We shall now consider the principal features of the influence of the substituents which are of general importance for the structure–property relations involving organosilicon compounds.

Table 3. Correlation of spectroscopic characteristics.

No.	Compound	Quantity correlated	Eqn.	A_0	ρ^*	r(R)	n	Remarks	Refs.
				From infrared spectra					
1	R_3SiH	ν(SiH), cm^{-1}	(1)	2106	17.5	—	22	R = any substitutent	60, 61
2	Ditto	ν(SiH), cm^{-1}	(1)	2115	31.5	0.94	43	R = H, alkyl, or substituted alkyl; s = 8.7	62, 63—65
3	»	ν(SiH), cm^{-1}	*	2141	24.4	0.99	43	a = −3.83; s = 3.7; R = ditto	62
4	»	ν(SiH), cm^{-1}	**	2110	24.5	0.99	43	a = 11.0; s = 2.7; R = ditto	66
5	$R_3SiOSi(Me_2)H$	ν(SiH), cm^{-1}	(1)	2117	8.1	0.91	9	s = 1.3; R = alkyl, substituted alkyl, or Ph	67
6	XR_2SiH, X=Cl	ν(SiH), cm^{-1}	(1)	2089	25.8	0.95	8	s = 5; R = H, alkyl, or substituted alkyl	68
7	Ditto, X=Ph	ν(SiH), cm^{-1}	(1)	2094	41	0.99	7	s = 2.2; R = ditto	68
8	Ditto, X=Vin	ν(SiH), cm^{-1}	(1)	2091	46	0.99	5	s = 3.6; R = ditto	68
9	X_2RSiH, X=Cl	ν(SiH), cm^{-1}	(1)	2053	26.5	0.94	6	s = 5.3; R = ditto	68
10	Ditto, X=Ph	ν(SiH), cm^{-1}	(1)	2074	42	0.99	3	R = ditto	68
11	$R_nX_{3-n}SiH$ (n=0, 1, 2), X=Cl	ν(SiH), cm^{-1}	(1) σ(Si)	2118	26.9	0.99	16	s = 4.6; σ(Si) for Cl = 1.69; σ(Si) = σ^* for "normal" substituents	68
12	$R_nX_{3-n}SiH$ (n=0, 1, 2), X=Ph	ν(SiH), cm^{-1}	(1) σ(Si)	2115	41	0.99	12	s = 1.6; σ(Si) for Ph = 0.09	68
13	ditto, X=Vin	ν(SiH), cm^{-1}	(1) σ(Si)	2114	45.5	0.99	7	s = 2.8; σ(Si) for Vin = 0.15	68
14	R_3SiH	$10^{-4}A^{0.5}$(SiH_2), litre mol^{-1} cm^{-2}		1.35	−0.19	0.93	12	R = alkyl or substituted alkyl; A = integral intensity	65, 69, 70—72,
15	R_2SiH_2	$10^{-4}A^{0.5}$(SiH), litre mol^{-1} cm^{-2}	(1)	1.72	−0.12	0.92	7	R = alkyl or substituted alkyl	73
16	R_3SiPh	ν(C–H) for phenyl, cm^{-1}	(1) (σ_1)	3071	5.57	—	12	s = 0.9; R = any substituent	74
17	R_3SiF	ν(Si–F), cm^{-1}	(1)	889	147	0.96	8	R = alkyl or benzyl	40, 75
18	$HC{\equiv}C(Me)_2SiOR$	$\Delta\nu$(SiOC), cm^{-1}	(1)	0.15	0.66	0.99	5	R = alkyl	76
				From NMR spectra					
19	R_3SiH	τ(H–Si), p.p.m.	(1)	6.16	−0.29	0.99	16	R = H, alkyl, substituted alkyl, Cl, Ph, or m-$CF_3C_6H_4$	61
20	Ditto	J (^{29}SiH), Hz	(1)	−203.4	19.76	0.97	63	s = 11; R = any substituent	77, 78
21	Ditto	J (^{29}SiH), Hz	***	−181	−12.9	0.98	63	ρ_1^* = −2.9; s = 8.7; R = any substituent	77
22	$R_3SiOSi(Me_2)H$	J (^{29}SiH), Hz	(1)	−203.4	−2.9	0.97	8	s = 0.24; R = alkyl or substituted alkyl	67
23	R_nSiMe_{4-n}	τ(CH_3), p.p.m.	(1)	10.0	−0.14	0.94	26	R = H, alkyl, substituted alkyl, or Cl	61, 79, 80
24	R_nSiEt_{4-n}	τ(CH_2), p.p.m.	(1)	9.38	−0.085	0.96	6	R = ditto	80
25	R_3SiOEt	τ(CH_3 in OEt), p.p.m.	(1)	8.87	−0.077	0.92	6	R = alkyl, substituted alkyl, or Ph	81
26	$R_2Si(OEt)_2$	τ(CH_3 in OEt), p.p.m.	(1)	8.88	−0.039	0.99	10	R = ditto	81
27	$RSi(OEt)_3$	τ(CH_3 in OEt), p.p.m.	(1)	8.92	−0.038	0.99	9	R = ditto	81
28	R_3SiOEt	τ(CH_2 in OEt), p.p.m.	(1)	6.41	−0.138	0.99	6	R = ditto	81
29	$R_2Si(OEt)_2$	τ(CH_2 in OEt), p.p.m.	(1)	6.42	−0.104	0.99	10	R = ditto	81
30	$RSi(OEt)_3$	τ(CH_2 in OEt), p.p.m.	(1)	6.53	−0.101	0.99	9	R = ditto	81
31	$RSi(OCH_2CH_2)_3N$	τ(H_2CO), p.p.m.	(1)	6.23	−0.180	0.98	6	R = H or alkyl	82
32	ditto	τ(H_2C), p.p.m.	(1)	7.21	−0.177	0.97	6	R = ditto	82
33	Me_3SiOR	δ (^{29}Si), p.p.m.	(1)	14.88	8.11	0.98	20	R = alkyl or substituted alkyl	50
34	ditto	δ(^{29}Si), p.p.m.	(1)	14.87	5.21	0.98	11	R = Ph or substituted aryl	83
35	$Me_3SiOCOR$	δ (^{29}Si), p.p.m.	(1)	15.14	4.73	0.99	10	s = 0.46; R = alkyl or substituted alkyl	83
36	$R_3Si^1OSi^2(Me_2)H$	δ ($^{29}Si^2$), p.p.m.	(1)	−7.83	4.83	0.99	8	s = 0.28; R = ditto	67
37	$R(Me)SiO(Me_2SiO)_2$	$\Delta\delta$ (^{29}Si), p.p.m.	(1)	—	1.64	0.94	6	s = 0.25; R = ditto	84
38	$YCH_2Si(OCH_2CH_2)_3N$	δ (^{29}Si), p.p.m.	(1)	−67.1	−11.3	0.99	8	s = 0.77; Y = alkyl or substituted alkyl	85
39	$YCH_2Si(OEt)_3$	δ (^{29}Si), p.p.m.	(1)	−45.3	−11.3	0.99	8	s = 1.28; Y = ditto	85
40	R_3SiF	τ(^{19}F), p.p.m.	(1)	44.0	−60	0.99	8	R = alkyl	75
41	R_2SiF_2	τ(^{19}F), p.p.m.	(1)	63.4	−60			R = alkyl	86
42	R_3SiNR_2' и NH_3	τ(^{14}N), p.p.m.	(1)	383.7	−36.7	0.98	7	R = alkyl or alkoxy-group; R' = H or R_3Si	87
				From NQR spectra					
43	R_3SiCl	ν_m^{77}(^{35}Cl), MHz	(1)	16.63	0.404	0.96	30	s = 0.11; R = H, alkyl, substituted alkyl, Ph, or Vin	88, 89, 90
44	R_2SiCl_2	ν_m^{77}(^{35}Cl), MHz	(1)	17.77	0.415	0.99	11	s = 0.08; R = ditto	88, 89
45	$RSiCl_3$	ν_m^{77}(^{35}Cl), MHz	(1)	18.91	0.484	0.96	12	s = 0.09; R = ditto	88—90
46	R_3SiCH_2Cl	ν_m^{77}(^{35}Cl), MHz	(1)	34.05	0.308	0.98	21	s = 0.18; R = any substituent	91
47	$R_3SiCHCl_2$	ν_m^{77}(^{35}Cl), MHz	(1)	35.28	0.279	0.99	5	s = 0.02; R = Me, Cl, or Ph	91
48	R_3SiCCl_3	ν_m^{77}(^{35}Cl), MHz	(1)	37.59	0.166	0.95	5	s = 0.21; R = Et, $PhCH_2$, Cl, OEt, or Ph	91
49	R_3SiBr	ν_m(^{81}Br), MHz	(1)	113.1	3.95	—	5	s = 0.81; R = alkyl, Ph, Cl, or Br	92

The following equations have been used respectively:

*$\nu_i = \nu_0 + \rho^* \sum\sigma^* + a \sum(n_H + 0.4n_C)$;

**$\nu_i = \nu_0 + \rho^* \sum\sigma^* + aq$, where $q = 0-3$ is the number of silicon hydride bonds combined with the "indicator" Si–H bond;

***$J = J_0 + \rho^* \sum\sigma^* + \rho_1^* (\sigma_1^*\sigma_2^* + \sigma_2^*\sigma_3^* + \sigma_1^*\sigma_3^*)$.

III. SPECIFIC FEATURES OF THE EFFECTS OF SUBSTITUENTS AT THE SILICON ATOM

1. The Inductive Effect

The vast majority of the relations presented in Tables 1–3 demonstrate the exclusive influence of the inductive effect of the substituents. In this respect organosilicon compounds exhibit a much greater similarity to normal organic compounds than to organic derivatives of phosphorus. Indeed, the inductive Taft σ^* constants cannot be used for the ρ,σ analysis of organophosphorus compounds owing to the considerable resonance influence of many substituted alkyl groups. As a result, whereas the Kabachnik constants σ^f for unsubstituted alkyl groups are proportional to their σ^* constants, for substituted alkyls (and substituents capable of p_π–d_π conjugation with phosphorus), the constant σ^f reflects both the inductive (σ^f_I) and resonance (σ^r_R) influence of the substituent:

$$\sigma^f = \sigma^f_I + \sigma^f_R .$$

The resonance effect of the substituted alkyls in organophosphorus compounds (and in derivatives of other elements having d orbitals available for bonding[110]) has been explained by an intramolecular interaction, for example, of the following type[7]:



Such bonding is possible, in principle, also in silicon compounds; nevertheless its manifestation is not typical in this instance, which has been confirmed by numerous relations involving only the Taft σ^* constants for a wide variety of unsubstituted and substituted alkyl groups. The data for the "α-effect", which will be examined below, constitute an exception.

On the other hand, the relations for compounds with substituents capable of p_π–d_π interaction deviate as a rule from the relations based on the σ^* constants of other substituents (for further details, see below). At the same time, examples (Table 3, Nos.16, 20, and 21) of the dependence of certain properties solely on the inductive effect have been described in the literature for compounds with any substituents at the silicon atom. Relations Nos.20 and 21 have been most completely confirmed experimentally for the spin–spin coupling constants $J(^{29}SiH)$ for molecules of silicon hydrides on the basis of ^1H NMR data. These data are also consistent with theoretical ideas, according to which the extent of the short-range spin–spin interaction is determined mainly by the amount of s character of the corresponding bond[111]. The above relations are therefore suitable for the estimation of the inductive constants of any non-trivial substituents at the silicon atom, for which the literature values of the Taft constant are not available[77,112].

2. The Influence of the Steric Effect

The extreme rarity of the manifestation of the steric effect in reactions of organophosphorus compounds is most likely to be due to the fact that the most readily available derivatives containing the compact phosphoryl groups were used in most of the investigations. However, if the compound has three organic substituents at the phosphorus atom, their steric influence on the reactivity is in some cases fairly appreciable[7].

In contrast to organophosphorus compounds, compounds with three or even four organic substituents at the silicon atom have been frequently synthesised even more readily than their organic analogues. Therefore the majority of the reactions of organosilicon compounds investigated at the level of ρ,σ analysis have been carried out using derivatives with a strongly shielded silicon atom. The influence of the steric effect of substituents at the silicon atom on the reactivity of a wide variety of organosilicon compounds has been discussed very widely in the literature at a qualitative level. Certain generalisations in this field are described in Sommer's monograph[17].

The quantitative data presented in Table 1 demonstrate a significant manifestation of the steric influence of substituents in many reactions of compounds of the type R_3SiX and even R_2SiX_2 (R = organic substituent and X = functional group). Not a single case of correlations which do not take into account the steric effect has been described for compounds with tertiary substituents at the silicon atom. There are a few instances of such relations describing compounds with substituents having the isostructure (Table 1, Nos.6, 7, 16, 29, and 33). On the other hand, the data for some reactions of compounds with substituents having the normal structure were interpreted successfully solely in terms of an equation taking into account the steric effect (Table 1, Nos.5, 26 and 28).

The role of the steric effect diminishes as bulky substituents move further away from the reaction centre. Thus the logarithms of the equilibrium constants for the alcoholysis of trimethylacyloxysilanes $Me_3SiOCOR$, in which the substituent R is separated from the silicon atom by the group OC(O), are linearly related to the $\sigma^*_{R_i}$ for any R, including R = t-Bu (Table 1, No.20). In the remaining cases the correlations for reactions of triorganylsilanes with functional groups, which do not take into account the steric factor, are most likely to be because compounds with substituents whose steric effects differed little were used in the investigations rather than to the low value of the steric factor. This hypothesis is supported by the finding that the majority of the reactions in Table 1 are characterised by a weak inductive effect of the substituents (low values of the reaction constant ρ^* in the Taft equation), which is the reason for the increased importance of other effects, including the steric effects, taken into account by any multiple correlation.

As for a number of organic compounds, the reactions of organosilicon derivatives involving acid catalysis are characterised by a much weaker influence of the inductive effect and a much stronger influence of the steric effect of the substituents than the analogous processes under the influence of a basic catalyst. Thus, although the values of $\lg k_{rel}$ for the triethylamine-catalysed condensation of diorganylsilanediols in methanol are related to the values of $\sum \sigma^*$ of the diorganyl groups by a single-parameter equation with the reaction constant $\rho^* = 4.7$ (Table 1, No.25),[32] the equation proved to be unsuitable for the analogous reaction in the presence of HCl.[33]

The result of our treatment of the data of Dejak et al.[33] in terms of an equation taking into account both $\sum \sigma^*$ and $\sum E^c_s$ (Table 1, No.26) confirmed the hypothesis of Dejak et al.[33] concerning the decisive role of the steric factor in this reaction. The results of studies[8,10] of the kinetics of the acid and alkaline solvolysis respectively of triorganylsilanes with n-alkyl, fluoroalkyl, and cyanoalkyl substituents

were evaluated from the relation between $\lg k_i$ and $\sum \sigma_i^*$ (Table 1, Nos.1 and 4). The value of ρ^* for alkaline solvolysis (4.42) proved to be much higher than for acid solvolysis (0.77). However, in both cases there were appreciable deviations of the points corresponding to compounds with more bulky substituents. The experimental data[9] for the reactions indicated (without the corresponding results for compounds with fluoro- and cyano-alkyl groups, for which literature values of the steric constants are not available) were interpreted in terms of Eqn.(2), which takes into account both the inductive and steric effects of the substituents. As a result, the two-parameter correlation for the basic solvolysis made it possible to describe by a single relation a series of points differing appreciably from the theoretical values obtained with the aid of their inductive effects of the substituents alone (Table 1, No.5). Statistical treatment of the experimental data for the analogous acid solvolysis reaction showed that the rate of the process is almost wholly determined by the steric effect of the substituents (Table 1, No.2).[9]#

An analogous conclusion has been reached[20] for the hydrosilylation of hex-1-yne by triorganylsilanes (Table 1, No.14). However, in this study too a very narrow statistical selection was made (only six points were chosen for the calculation) and there are deviations of the points for Et_3SiH, Pr_3SiH, and $Me_2(Me_3CCH_2)SiH$ which cannot be accounted for by the proposed relation. Since instances of the dependence of the reaction rate exclusively on the steric effect of the substituents are extremely rare in correlation analysis, the above examples merit additional investigation.

3. The Influence of the Hyperconjugation Effect

Apparently owing to the abundance of different substituents containing C–H bonds at the silicon atom, many more data which can be interpreted as due to the manifestation of the hyperconjugation effect (in the given case σ,d conjugation) have been obtained for organosilicon compounds than for phosphorus derivatives. In particular, it is believed that, precisely because of the displacement of the electrons of the C–H bonds to the d orbitals of the silicon atom, the C–Si bond is unusually weakly polarised and is chemically inert[114]. The stabilisation of the C–Si bond by σ,d hyperconjugation has been confirmed by theoretical calculations[115,116].

Quantitative allowance for the hyperconjugation effect in the determination of the reactivity of organosilicon compounds has been based solely on kinetic data for the reactions of organylsilanes with methylphosphonic acid (Table 1, No.15). In order to establish a correlation, use was made of points for eight compounds having the general formula RMe_2SiH with n-, iso-, and s-substituents as well as R = cyclohexyl. The deviation of the point for the t-butyl derivative was explained by the "saturation of hyperconjugation", i.e. by a decrease of the sensitivity of the rate of reaction to a change in the number of α-C–H bonds with increase of the latter[21].

The authors[21] (Table 1, No.9) found that the points for the compounds R_3SiH (R = $PhCH_2$ or n-alkyl but not Me) and MeR_2SiH form two parallel lines on the $\lg k_i - \sum \sigma_i^*$ diagram. Their relative positions suggested an increased influence of the hyperconjugation effect for methyl derivatives. The facts that the Me_3SiCH_2 group ($\sigma^0 = -0.20$) is significantly more electropositive than the Me_2Si group ($\sigma^0 = 0.04$) [117] and that the Et_3SiCH_2 group is less electropositive than the Me_2SiCH_2 group ($\sigma^* = -0.13$ and -0.26 respectively) constitute very important arguments in support of the occurrence of hyperconjugation[118].

The interpretation of certain spectroscopic properties of organosilicon compounds also supports the hyperconjugation effect. Infrared spectroscopic data for organylsilicon hydrides are particularly characteristic. The values of ν_i(SiH) for compounds in the R_3SiH, R_2SiH_2, and $RSiH_3$ series (R = alkyl or substituted alkyl) form three parallel lines on the correlation diagram in terms of $\sum \sigma^*(R)$.[63,64] The authors explained this finding by the different contributions of the hyperconjugation effect depending on the number of alkyl substituents at the silicon atom. The individual correlations for a series of compounds with n- or iso-groups can apparently also be accounted for by the differences between the hyperconjugation components[65]. It has been shown[62] (Table 3, No.3) that the data for all the above organylsilicon hydrides can be described by a general relation taking into account the effect of hyperconjugation. However, we should note that, when there are substituents capable of $p_\pi - d_\pi$ interaction at the silicon atom ($R_nX_{3-n}SiH$, R = H, alkyl, or substituted alkyl, X = Cl, Ph, or Vin, and $n = 1$ or 2), the hyperconjugation effect is not exhibited (Table 3, Nos.6–10). This finding was explained by competition between the substituents R and X for the *d* orbitals of the silicon atom, as a result of which the stronger $p_\pi - d_\pi$ conjugation predominates[68].

There are also certain differences between the parameters of the correlations of the integral intensities of the Si–H bond absorption bands and the Taft constants for a series of compounds differing in the structure of the alkyl substituents at the silicon atom[65] or the number of Si–H bond in the molecule[69] (Table 3, Nos.14 and 15). Plots of $\Delta A_i^{0.5}$ against $\sum \sigma_p$ for the organylsilicon hydrides $R_nX_{3-n}SiH$ (R = alkyl, X = Cl, Ph, or XC_6H_4, and $n = 0$, 1, or 2) give rise to three lines with identical slopes for a series of compounds differing in the values of *n*. It is believed[65] that the distances between the lines for the X_3SiH series and the lines for RX_2SiH or R_2XSiH characterise the magnitude of the effect of the σ,d conjugation of one or two alkyl groups respectively with the silicon atom[71].

4. The Influence of the α-Effect

We shall now consider recent data concerning the α-effect in certain α-substituted alkylsilanes, mainly chloromethyl derivatives. In the majority of correlations of the properties of organosilicon compounds the influence of substituents of the type CH_nCl_{3-n} as well as other substituted alkyls is successfully taken into account by the usual σ^* constant. This applies to the reactivities[30,32–37,42] and ^1H NMR data for organylethoxysilanes[81] and organylmethylsilanes[79], the relative basicities of hexaorganyldisiloxanes, triorganylethoxysilanes[45], organyltriethoxysilanes, and organyltrimethoxysilanes[46], the infrared spectra (position[62] and intensity[69] of the absorption band due to the Si–H bond) of organylsilicon hydrides, and the NQR spectra of many organylchlorosilanes[88,91].

Later this relation was used to estimate the steric effects of certain non-trivial substituents at the silicon atom[113].

Furthermore, for a number of existing examples the apparent "anomaly" of the properties of compounds with α-chloroalkyl substituents, which has been usually attributed to the α-effect, has been either inadequately rigorously demonstrated or an alternative explanation is possible. Thus the unduly low reactivity, from the standpoint of relation No.1 (Table 1), of chloromethyldimethylsilane has been explained in a study of the acid hydrolysis of organylsilicon hydrides[8] by the presence of the resonance structure $^{+}ClCH_2=Si^{-}\leftrightharpoons$. However, it was found later[9] that the point for this compound does not deviate from the general relation taking into account the steric constants of the substituents (Table 1, No.2).

The relations between $\lg k_i$ and $\sum \sigma_i^*$ proposed[13,15] for the ozonisation and bromination reactions respectively do not describe a greater number of points than the number of points which deviate appreciably from them (the latter include the points for compounds with α-chloroalkyl substituents). The use of these relations for the construction of mathematical models of the corresponding processes is therefore problematical. Consequently the authors' conclusions[13,15] concerning the manifestation of the α-effect are not sufficiently well founded.

In the infrared spectra of organylsilicon hydrides with a chloromethyl group the absorption band due to the Si–H bond is frequently an unresolved doublet. The average value of ν(SiH) fits on the existing relations without deviations (Table 3, Nos.2–4). The presence of the doublet has been explained[119,120] by the equilibrium between the inner-complex (α-effect) and the usual forms of the molecules of the compounds indicated. However, this view has been criticised[121] and the phenomenon has been attributed to the presence of conformational isomers.

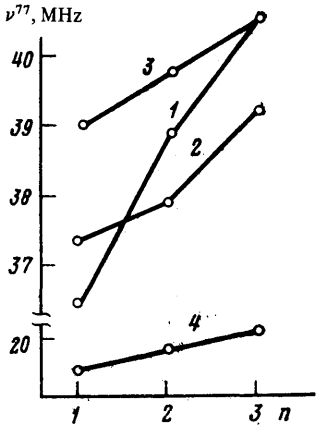


Figure 1. Relation between the ^{35}Cl NQR frequency (ν^{77}) for the molecules of the $ECl_3CCl_nH_{3-n}$ series (E = C or Si) and the number of chlorine atoms n: *1*) in the CCl_nH_{3-n} group with E = C; *2*) ditto with E = Si; *3*) in the CCl_3 group; *4*) in the $SiCl_3$ group[123].

The most extensive data on the properties of chloromethyl derivatives of silicon, attributed to the influence of the α-effect, have been obtained by NQR. As already mentioned above, the points for compounds with such substituents fit without deviations on the correlations between the values of ν_m^{77} and $\sum\sigma^*$ for the series of compounds RR'R"SiCl, where R is an organic substituent and R' and R" are organic substituents or Cl (Table 3, Nos.43–45), and for compounds $RR'R''SiCH_nCl_{3-n}$, where R, R', and R" are organic substituents, halogens, and alkoxy or siloxy-groups, and $n = 0$, 1, or 2 (Table 3, Nos.46–48). The following facts have been attributed to the manifestations of the α-effect. Despite the lower electronegativity of the silicon atom compared with the carbon atom, which presupposes lower Taft constants for substituents in compounds involving silicon, in the $R_3ECH_nCl_{3-n}$ series, where E = Si or C, the quantity ν_m^{77} for compounds with E = Si and low values of $\sum\sigma^*(R_3)$ is greater than in the case where M = C.[91,122–124]. Accordingly, of one begins with the relation between ν_m^{77} and σ* for the RCl series ($\nu_0 = 33.2$ and $\rho^* = 2.7$) [125], it is found that unusually high values of the σ* constant for the R_3SiCH_2 groups correspond to the experimental values of ν_m^{77} for the compounds R_3SiCH_2Cl. For example, $\sigma^* = 0.4$ has been calculated for the Me_3SiCH_2 group, in contrast to $\sigma^* = -0.26$ in handbooks. This phenomenon is characteristic precisely of α-derivatives, since the values of ν_m^{77} for the $R_3E(CH_2)_nCl$ series are higher in the case where E = Si only when $n = 1$ but not when $n = 0$, 2, or 3.[122]

The specific features of the NQR of chlorine in the Si–C–Cl group are clearly shown when the frequencies ν_m^{77} for compounds in the $CCl_3CCl_nH_{3-n}$ and $Cl_3SiCCl_nH_{3-n}$ series are compared (Fig.1). Whereas the frequencies for the chlorine atoms attached to the silicon in the $SiCl_3$ group are significantly lower than the corresponding frequencies $\nu_m^{77}(CCl_3)$ in the $CCl_3CCl_nH_{3-n}$ series (as might have been expected in view of the influence of the electropositive silicon), the frequencies for the groups $ECCl_nH_{3-n}$ with E = Si or C differ much less, which indicates the operation of the α-effect in the silicon-containing fragment[123]. The authors[123] also see the manifestation of the α-effect in the observation that the slope ρ* in the Taft equation for compounds of the R_3CCl series without silicon (1.02) is significantly higher than for the organosilicon series $RR'(X_3Si)CCl$ (0.42). However, this view can be contrasted with the finding that the values of ρ* found from the analogous relation for organic derivatives are higher than for organosilicon derivatives also in the R_3ECl series (E = C or Si) where the conditions for the manifestation of the α-effect do not exist.

Thus examination of all the data for the "unusual" properties of compounds with the Si–C–Cl group shows that the most convincing evidence has been obtained with the aid of NQR–in the form of increased NQR frequencies for organosilicon compounds compared with their carbon analogues. However, the interpretation of the findings as a manifestation of intramolecular coordination has aroused objections by Mel'nikova et al.[126] in this case also, although they do not propose any alternatives. They believe[126] that the interaction in the Si–C–Cl group within the complex can be exhibited only when other highly electronegative substituents are present at the silicon atom, while according to NQR data the greatest anomaly is shown for the region of low values of σ*.

In the study of correlations for other carbon-functional organosilicon compounds with Si–C–X groups, where X is an atom with an unshared electron pair, instances of deviations due to intramolecular coordination were still more infrequent.

Thus the "unusually" large value of $\Delta\nu(OH) = 318$ cm^{-1} in the infrared spectrum of a mixture of phenol with $(Me_3SiCH_2)_2O$, initially attributed to the influence of the α-effect[127], was later shown to be satisfactorily accounted for by the relation $\Delta\nu_i = 263 - 90\ \sum\sigma_i^*$ for ethers[44] using $\sigma^*\ (Me_3SiCH_2) = -0.26$.

The higher reactivity of $Me_3SiCH_2OSiMe_3$ ($k_{rel} = 0.15$) compared with $Me_3CCH_2OSiMe_3$ ($k_{rel} = 0.049$) in the ethylamine-catalysed methanolysis of compounds in the series $R(CH_2)_nOSiMe_3$ has been explained by the intramolecular interaction between the Si and O atoms in the Si–C–O group[24]. For analogous compounds with $n = 2$, 3, or 4, the reaction rates are approximately the same. However, since the rate of this reaction is influenced appreciably by the steric effect of the substituents R (Table 1, No.19), a final conclusion concerning the causes of the feature noted above can be reached only after taking into account the steric hindrance due to the Me_3SiCH_2 group, the steric constant of which has not been determined so far.

The dependence of the values of $\Delta\nu(OH)$ in the infrared spectra of complexes of phenol with trimethylalkoxysilanes on the inductive constants has been described[50] by a quadratic equation (Table 2, No.9). The points for compounds with bulky substituents (Me_3C and Me_3CCH_2) and also CH_2Cl deviate from this relation. The electronegativity of the chloromethyl group, which is apparently unusually low from the standpoint of this relation, has been explained by a "specific" redistribution of electron density in the Si–O–C–Cl group. However, if the interpretation is based on the usual linear relation (Table 2, No.10), which is statistically quite reliable ($r = 0.94$ when the point for the compound with the sterically bulky group CH_2CCl_3 is disregarded), then the result for Me_3SiOCH_2Cl no longer appears to be anomalous.

We shall consider finally the data for the characteristic features of the properties of compounds with the Si–C–N group. The basicity constants of *N*-substituted cyclic amines having the general formula $R\overline{N(CH_2)_{m-2}CH_2}$, where $m = 6$ [129,130], 5, or 7 [118], and R = organic substituent, or $R'_3Si(CH_2)_n$ ($n = 1$, 2, or 3 and R′ = alkyl) have been determined. Individual correlations $(pK_a)_i = (pK_a)_0 + \rho^*\sigma_i^*$ have been found for each heterocycle from data for organic derivatives (except for $R = Me_3CCH_2$, which deviates). The values $\sigma^*(Me_3SiCH_2) = -0.17 - -0.18$ calculated from these relations differ appreciably from the literature value $\sigma^* = -0.26$. The difference (which, however, is significantly smaller than that obtained on the basis of NQR data for the chloromethyl substituent—see above) was explained[130] by the manifestation of the α-effect in the Si–C–N group. This difference is not associated with the steric effect of the Me_3SiCH_2 group, because it is independent of the size of the heteroring of the amine, while the analogous difference for the neopentyl group increases with *m* and hence with enhancement of the steric hindrance in the molecule.

In contrast to these data, the basicity of $Me_3SiCH_2NR_2$ (R is an organic group) hardly differs from that calculated from the relation for organic amines R_3N, namely $(pK_a)_i = 7.86 + 2.7\ \sum\sigma^*$ using the usual value $\sigma^*(Me_3SiCH_2) = -0.26$.[57]

The data considered here show that the anomalies for compounds with the Si–C–X group, which have been reliably established from the standpoint of ρ,σ analysis and which can be attributed to the α-effect, have been observed only for a very small number of compounds, so that further studies in this field are of interest. Furthermore, the question why the resonance interaction is shown much more weakly and rarely for a series of substituted silicon alkyls than for the corresponding phosphorus derivatives still awaits an answer.

5. The Influence of the p_π–d_π Effect

Although the problem of the p_π–d_π interaction in organosilicon compounds has been actively discussed already for several decades[114,131–133], no general solution whereby a quantitative account could be taken of this effect have so far been proposed.

In organophosphorus compounds, the effect of the p_π–d_π interaction can be taken into account for a wide range of substituents with the aid of the resonance constants σ_R^f.[7] The method used by Mastryukova and Kabachnik[7] to find these constants is of general validity for the estimation of resonance contributions[1–3] and consists in the determination of the difference between the real value of the measured quantity and the value calculated on the assumption that only the inductive effect of the substituent operates. This approach involves a series of assumptions. In particular, it is assumed that the resonance effect is additive and the influence of other substituent effects (steric, hyperconjugation, etc.) is neglected. The corresponding correlation equation using the Taft constants and the resonance constants σ_R is

$$A = A_0 + \rho^*\sigma^* + \rho_R\sigma_R, \qquad (3)$$

where ρ_R is a proportionality coefficient taking into account the sensitivity of the given property to the resonance effect of the substituents; for the standard series, it is assumed that $\rho_R = 1$.

It is noteworthy that attempts have been frequently made to isolate by an analogous procedure the contribution of the resonance effect (due to the p_π–d_π interaction) of individual substituents in organosilicon compounds[13,36,41,134–136], but the results obtained did not lead to the derivation of universal organosilicon resonance constants. A critical analysis of these attempts is described below: at present we shall consider the problem of the applicability of the traditional approach to the estimation of the resonance effects of substituents at the silicon atom.

In the first place we shall attempt to test the validity of the additive rule. For this purpose, it is in principle sufficient to analyse data for the properties of a series of compounds with a variable number of certain identical substituents capable of p_π–d_π interaction, for example, a series of the type $Me_{3-n}X_nSiY$, where X is a substituent, Y is a functional group, and $n = 0$–3. For this series, the dependence of the property on the number *n* of substituents X is expressed by the equation

$$A_n = n\rho_n(\sigma^* + \sigma_R^{Si}), \qquad (4)$$

where σ_R^{Si} are the resonance constants of the substituents in the organosilicon compounds. Here the values of σ_R^{Si} were taken without correction for the slope ρ_R, because each of these microseries can be regarded as standard. Under the condition where the given property is not influenced by the effects of the substituent X and the CH_3 group, which were not taken into account in Eqn.(4), a linear relation between A_n and $_n$ implies that σ_R^{Si} remains constant regardless of the number of substituents X in the molecule.

Such linear relations have been obtained for the compounds $Me_{3-n}X_nSiH$ ($n = 0$–3, X = Ph, Cl, Br, NMe_2, C ≡ CH [137], or Vin [137,138]) from the values of ν(SiH) in the infrared spectra, for $Et_{3-n}X_nSiH$ ($n = 0$–3) with X = Ph from the relative ozonolysis rate constants[12] or with X = Vin from the solvolysis rate constants (95% EtOH) [138], for $Me_{3-n}Cl_n$·.SiOR ($n = 0$–3, R = Et or iso-Pr) [51] and $Me_{4-n}Si(OR)_n$ ($n = 1$–4, R = Me, Et, Pr, or iso-Pr) [139] from the Δν(OH) in

the infrared spectra of the complexes of these compounds with phenol, for $Me_{3-n}Cl_nSiVin$ ($n = 0-3$) from the relative rate constants for the addition of the $Cl_3C^\bullet$ radical [109], for $Me_{3-n}Cl_nSiCH_2C_6H_5$ ($n = 0-3$) from the relative chlorination rate constants[140], for $Et_{4-n}X_nSi$ ($n = 0-3$) with X = Cl [80,105] or Br [105] and for $Me_{3-n}Cl_nSiOEt$ ($n = 0-3$) [81] from the values of $\tau(CH_2)$ in ^1H NMR spectra, and for $Me_{3-n}X_nSiVin$ ($n = 0-3$, X = Cl, MeO, or Me_3SiO; $n = 0$, 1, or 2, X = Ph; $n = 0$, 2, or 3, X = OEt) from the relative rate constants for their reactions with thioacetic acid[42].

At the same time it has been found that there is no linear relation for compounds in the series $Me_{4-n}Si(OPh)_n$ ($n = 1-4$) on the basis of the $\Delta\nu$(OH) in the infrared spectra of their complexes with phenol[141], for $Me_{4-n}Si(OEt)_n$ ($n = 1-4$) on the basis of the values of $\tau(CH_2)$ and $\tau(CH_3)$ in the ^1H NMR spectra[81], for $Me_{3-n}F_nCH_2Ph$ ($n = 0-3$) on the basis of the relative rate constants for their chlorination[142], for $Et_{3-n}Cl_nSiH$ ($n = 0-3$) and $Pr_{3-n}(OEt)_nSiH$ ($n = 0-3$) on the basis of the rate constants for their addition to hex-1-ene[143], for $Me_{3-n}(Me_3SiO)_nSiH$ ($n = 0-3$) and $Pr_{3-n}\cdot(EtO)_nSiH$ ($n = 0-3$) on the basis of their solvolysis rate constants (95% EtOH) [144], and for $Me_{3-n}X_nSiH$ (X = F, MeO, or EtO), $Ph_{3-n}F_nSiH$, F_nSiH_{4-n} [137], and $Pr_{3-n}(EtO)_n\cdot SiH$ [143,144] ($n = 0-3$ throughout) on the basis of ν(SiH) in the infrared spectra.

The above list shows that almost all the substituents are capable of influencing additively the properties of the corresponding compounds. As regards the instances of a non-additive influence, one should bear in mind that the reactivity data did not take into account the steric influence of the substituents, which can distort the linear relation. In the remaining instances the absence of a linear relation is apparently caused by the non-additive influence of the electronic effects of the corresponding substituents (F and RO) when the latter accumulate in the molecule.

It would seem that these data permit the conclusion that Eqn.(3) is applicable at least to compounds with substituents which usually have an additive effect (Ph, Vin, Cl, and Br). However, there is an unexpected obstacle, which in fact has no analogies for compounds of other elements: in numerous instances the values of ρ^* in analogous correlations change on passing from the R_3SiY series to the $R_{3-n}X_nSiY$ series (X are substituents capable of p_π–d_π conjugation and R are other substituents). These cases are presented in Tables 2 and 3 (see Nos.2–4, 10–12, and 13–15 in Table 2 and 6–13 and 25–30 in Table 3). In view of the fundamental importance of this process, we shall consider the most typical results in greater detail.

Fig.2 presents the dependence of the chemical shifts of the methylene protons of the ethoxy-group on the values of $\sum\sigma^*$ for the remaining three substituents at the silicon atom in the molecules of organylethoxysilanes $R_{4-n}Si(OEt)_n$ (Table 3, Nos.28–30); the points for the $Me_{4-n}Si(OEt)_n$ series are indicated separately. Evidently the linear relation (4) for this series includes only points corresponding to $n = 2$, 3, or 4, but not $n = 1$. It is also seen that, owing to the difference between the slopes of the lines for the $R_{4-n}Si(OEt)_n$ series with $n = 1$, on the one hand, and for the series with $n = 2$ and 3, on the other, the distances between them are not constant. From the standpoint of the relation for the series of compounds with $n = 1$ (Table 3, No.28), the second and third ethoxy-groups therefore influence the chemical shift via the inductive effect, which formally diminishes on passing to the region of higher values of $\sum\sigma^*$. For example, the deviation calculated in terms of the σ^* scale from the above relation, caused by the influence of the excess ethoxy-group, is −0.43 for $Me_2Si(OEt)_2$ ($\sum\sigma^* = 1.37$) and −1.81 for $(Cl_3C)_2Si(OEt)_2$ ($\sum\sigma^* = 6.67$). Evidently, the difference between these values, each of which corresponds to the resonance effect of the ethoxy-group from the standpoint of Eqn.(3) is very considerable.

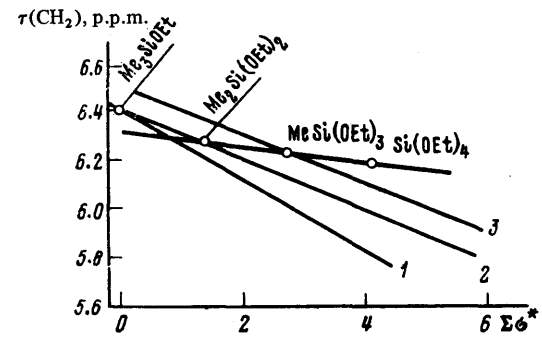


Figure 2. Dependence of the chemical shifts of the methylene protons of the ethoxy-group on the $\sum\sigma_i^*$ for the remaining three substituents at the silicon atom in the $R_{4-n}Si(OEt)_n$ molecules[81]: *1*) $n = 1$; *2*) $n = 2$; *3*) $n = 3$.

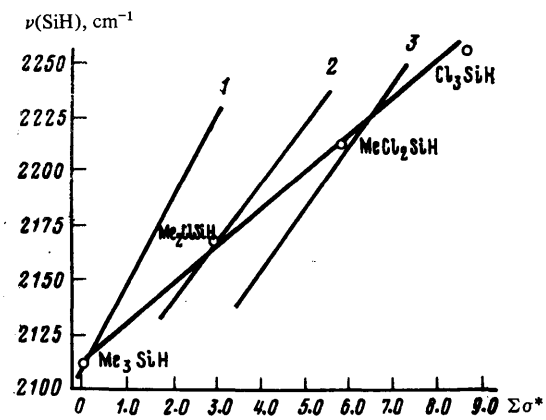


Figure 3. Dependence of ν(SiH) on σ_i^* for the substituents R_3 or $R_{3-n}Cl_n$ in the R_3SiH and $R_{3-n}Cl_nSiH$ molecules[68]: *1*) R_3SiH; *2*) R_2ClSiH; *3*) RCl_2SiH.

The individuality of the slopes of the straight lines corresponding to correlations for the series of compounds $R_{3-n}X_nSiH$ (Table 3, Nos.6–13), which differ in the type of substituent (X = Cl, Ph, or Vin), has been demonstrated[68] in relation to the dependence of the stretching vibration frequencies of the silicon hydride bond on the $\sum\sigma^*$ for the substituents at the silicon atom. An example of such relations for the case where X = Cl and their position on the graph relative to the regression line for the R_3SiH series (Table 3, No.2) are presented in Fig.3. Fig.3 also demonstrates the validity of Eqn.(4) for the $Me_nCl_{3-n}SiH$ microseries (when X = Ph or Vin, this relation also holds).

As in the previous instance, owing to the difference between the slopes of lines corresponding to the relations for R_3SiH and R_2XSiH, here the distances between the lines, caused by the influence of the substituent X, are not the same for the entire range of values of $\sum \sigma^*$.

Since the above study[68] is the only example hitherto where series of compounds with different substituents X have been investigated by a single method, it is of particular interest to analyse the nature of the variation of the slope of the relation between ρ^* and σ^* as a function of the nature of the substituent X. The data in Table 3 show that, when X = Ph or Vin, the quantity ρ^* is greater and, when X = Cl, it is smaller than in the correlation for the R_3SiH series. This corresponds formally to a decrease of the resonance influence of the substituents for X = Ph or Vin on ν(SiH) (i.e. the experimental values of ν_i approach those calculated from the relation for R_3SiH) and to an increase of the resonance influence of chlorine with increase of the values of $\sum\sigma^*(R_2X)$. Even if it is assumed that the change in the values of ρ^* is caused by the mutual influence of the inductive and resonance effects of the substituents in the molecules of R_2XSiH, it cannot therefore be taken into account by adding an additional term to the right-hand side of Eqn.(3). This is particularly true in view of the fact that, on further increase of the number of substituents X in the molecule, the slope no longer changes. Thus, so far one can only conclude that the coefficient ρ^* is specific to each substituent X; there are as yet insufficient data to formalise this phenomenon by a general correlation.

The results lead to the conclusion that in the general case the calculation of the constant σ_R^{Si} by Eqn.(3) is erroneous, because the calculated quantities are not constant for a specific substituent X and apparently do not reflect the true resonance contribution of the latter. A comparative estimate of random deviations (for different substituents X), corresponding to the quantity $\rho_R\sigma_R$ in Eqn.(3) [44,63,73,134–136,145–148], does not therefore appear to be sufficiently fruitful.

On the grounds that the values of ρ^* for the series of compounds $R_{3-n}X_nSiH$ with $n = 1$ or 2 and a constant X are virtually the same, the relations for the R_2XSiH series have been used as a basis for the estimation of the σ_R^{Si} and the deviations $\Delta\nu_i$ from these relations for compounds in the series RX_2SiH were attributed to the resonance influence of the second substituent X:

$$(\sigma_R^{Si}) = \Delta\nu_i/\rho_i^*.$$

The values of the resonance constant σ_R^{Si} found for the substituents X = Cl, Ph, and Vin were respectively −1.23, −0.51, and −0.50. The constants σ(Si), characterising the overall (effective) inductive effect of the substituents, were also calculated with the aid of the equation $\sigma^* + \sigma_R^{Si}$. Using the values of σ(Si) obtained [for substituents R which do not exhibit the resonance effect, $\sigma(Si) = \sigma^*$], the correlation parameters were calculated for the series of compounds $R_{3-n}X_nSiH$ with $n = 1$, 2, or 3 (Table 3, Nos. 11–13). The high accuracy of the correlations confirm the additivity of the resonance contribution of the substituents X independently of their number in the molecule. $\sigma_R^{Si}(OEt) = -1.06$ can be found analogously from the ^1H NMR data for the $R_2Si(OEt)_2$ and $RSi(OEt)_3$ series discussed above; $\sigma_R^{Si}(OMe) = -0.59 \pm 0.07$ has been found from data[11] for the methanolysis of the compounds $RSiH_2(OMe)$ and $RSiH(OMe)_2$. Other results suitable for estimates of this kind are so far not available in the literature.

It is seen from the preceding discussion that a fairly rigorous allowance for the p_π–d_π effect of the substituents at the silicon atom requires the use of extensive experimental data and is therefore difficult. Hence it is still useful to investigate the possibility of employing Eqn.(3), ignoring the possibility of a difference between the values of ρ^* for the R_3SiY and $R_{3-n}X_nSiY$ series, at least for an approximate comparative estimate of the extent of the p_π–d_π effects of different substituents. The only condition which ensures the possibility of applying the scale of approximate values of σ_R^{Si} obtained in this way is mutual proportionality of the influences of the p_π–d_π effect on any of the properties investigated. The validity of this condition makes it possible to use the slope ρ_R^* in Eqn.(3).

To test this claim, we shall consider the approximations obtained for the relative values of σ_R^{Si} [having assumed that $\sigma_R^{Si}(Cl) = 1$] in the case of the substituents Ph, Cl, or OEt, for which the greatest amount of factual data is available (Table 4). Table 4 shows that different research techniques manifest, as it were, a selective sensitivity to the influence of individual substituents, as a result of which a mutual proportionality of the changes in the resonance contribution does not obtain. Consequently the simplified approach to the establishment of a general relation proposed above is inapplicable. Hence it becomes clear why the values of σ_R^{Si} (or analogous quantities), frequently calculated in this way, have not been widely accepted.

Table 4. The relative values of σ_R^{Si} calculated by Eqn.(3) (for $\rho_R = 1$).

Compound and property investigated	R			References
	Ph	Cl	OEt	
$R_{3-n}X_nSiH$, i.r.s., ν(SiH)	0.32	1.0	0.41**	68,134*
$R_2XSiVin$ + AcSH, k_{rel}	0.13	1.0	0.51	42
$R_{3-n}X_nSiOEt$, $\tau(CH_2$ in OEt)	0.00	1.0	0.50	81*
$R_{3-n}X_nSiOEt$ + phenol, i.r.s., $\Delta\nu$(OH)	0.17	1.0	0.64	(45,51,149)*

*Calculated from data in the communications indicated.
**Here R = OMe.

Thus, although the very fact of the deviation from the relation for the R_3SiY series caused by the introduction of the substituent X in $R_{3-n}X_nSiY$ can serve as an indication of the manifestation of the p_π–d_π effect of the above substituent, the magnitude of the deviation is an extremely arbitrary characteristic of the magnitude of this effect. Furthermore, the same characteristic is not constant owing to the lack of proportionality in terms of the scales of the deviations obtained by different methods and for different models. The causes of such a significant difference in the manifestations of the resonance effects of the substituents in silicon and phosphorus compounds still remain obscure.

IV. THE ABILITY OF THE SILICON ATOM AND OF SILICON-CONTAINING ATOMIC GROUPS TO TRANSMIT EFFECTS

The transmission coefficient z_N of a structural unit N is defined[1-3] as the decrease of the inductive influence of the substituents R when the latter move away from the indicator centre Y as a result of the introduction of this particular structural unit. The values of z_N are determined from the ratios of the corresponding slopes or Taft constants:

$$z_N = \rho^*_{R-N-Y}/\rho^*_{R-Y} = \sigma^*_{R-N}/\sigma^*_R .$$

The few literature values of the transmission coefficients of organosilicon structural units as well as the values which we calculated from the literature data (with the aid of the $\rho^*-\rho^*$ method) are presented in Table 5. Evidently the transmission capacity of the silicon atom (Table 5, Nos.1–3) is not constant for different compounds, in contrast to the transmission capacity of organic structural units. This indicates differences between the mechanisms of the transmission of the inductive influence of substituents via a silicon atom. Presumably this is caused by the different extents of the $p_\pi-d_\pi$ interaction in different series. The unusually high transmission coefficient of the $SiCH_2$ group (Table 5, No.4) has been attributed[57] to an additional (apart from the σ-bond) interaction of the silicon and nitrogen atom. The coefficient $z_{OSi(Me_2)} = 0.15-0.26$ (Table 5, Nos.5 and 6) is entirely comparable to the transmission coefficient of the C–O bond ($z_{C-O} = 0.26-0.34$);[1] thus the abilities of the Si–O and C–O bonds to transmit the inductive effects of substituents are approximately the same.

Table 5. The transmission coefficients of the silicon atom and silicon-containing structural units.

No.	R-Y and R-N-Y series	Method of investigation and parameter investigated	$\rho^*_{(RY)}$	$\rho^*_{(RNY)}$	N	z_N	Refs.
1	ROR′ and R_3SiOEt	i.r.s., Δν(OH) for phenol	−90	−61	Si	0.68	44,45*
2	R-Cl and R_3SiCl	NQR, ν_m^{77}(^{35}Cl)	2.7	0.4	Si	0.15**	88,125*
3	R_2NH and $R_3SiNHMe$	kinetics of reaction with Ph_2SiH_2, k_i	—	—	Si	0.22	40
4	R_3N and $R_3SiCH_2NMe_2$	potentiometry, pK_a	−2.7	−1.8	$SiCH_2$	0.68	57
5	R_3SiH and $R_3SiOSi(Me_2)H$	^{1}H NMR, $J(^{29}SiH)$	19.8	2.9	$OSiMe_2$	0.15	67
6	Ditto	i.r.s., ν(SiH)	31.5	8.1	$OSiMe_2$	0.26	67

*Calculated from data in the communications indicated.
**The data for the RCl and R_3CCl series ($\rho^* = 1.02$) yielded $z_C = 0.37$, which is consistent with the literature value $z_{CH_2} = 0.36$.[125]

It is of interest to estimate the transmission capacity of the silicon atom compared with those of other elements in isostructural compounds. If the ρ^*/ρ^* method is used in this instance, it is possible to obtain a quantitative expression for the above estimate in the form of an "isostructural" transmission coefficient, which we shall designate by z':

$$z' = \rho^*(Si)/\rho^*(E),$$

where $\rho^*(Si)$ is the slope for the organosilicon series and $\rho^*(E)$ is the corresponding slope for the isostructural series in which silicon has been substituted by the element E. The values of z' calculated from the literature data are listed in Table 6.

Since the silicon atom is less electronegative than the carbon atom, its isostructural substituents should have a smaller inductive effect, which is reflected also in the values of z' for the silicon–carbon pair, the latter being always less than unity. However, a universal value of z' is also not observed, as for the coefficient $z(Si)$ discussed above. The inconstancy of the z' for compounds in which silicon is linked to a substituent capable of $p_\pi-d_\pi$ interaction (Table 6, Nos.1–3 and 7–9) apparently reflects the different degrees of manifestation of the resonance effect and for the series of compounds Nos.4–6 the different influences of the α-effect. It is of interest that a value $z' < 1$ has been obtained also for the Si/Ge pair (No.10), in which the germanium atom is less capable of $p_\pi-d_\pi$ bonding than the silicon atom despite being still less electronegative.

Table 6. The isostructural transmission coefficient z' for the silicon atom.

No.	Isostructural series*	Method of investigation and parameter investigated	ρ^{**} (M)	ρ^{**} (Si)	z'	Refs.
1	R_3MCl	NQR,	1.019	0.404	0.39	123
2	R_2MCl_2	ditto	0.959	0.415	0.43	123
3	$RMCl_3$	»	0.933	0.484	0.52	123
4	R_3MCH_2Cl	»	0.594	0.308	0.52	123
5	R_2MCHCl_2	»	0.409	0.279	0.68	91
6	R_2MCCl_3	»	0.408	0.166	0.41	91
7	$R_3MOH \cdot DMSO$	^{1}H NMR, chemical shift of H in HO(Hz)	73	65	0.89	58
8	$C_6H_5MR_3$	i.r.s., ν(CH) in C_6H_5	8.28	5.57	0.67	74*
9	$R(Me_2)MOR' \cdot PhOH$	i.r.s., Δν(OH) for phenol	−54	−47	0.87	49
10	$Rh_3SiOOMR_3 \cdot PhOH$	ditto	−33	−19.4	0.59	52

*M = C in Nos.1–9 and M = Ge in No.10.
**The constants σ_i were used by Knižek et al.[74] to calculate ρ^* (M, Si).

We may note finally the instances of the changes in the transition capacity of the silicon atom on passing from compounds R_3SiY to compounds $R_{3-n}X_nSiY$, partly discussed above. As already mentioned, the slope ρ^*, characterising the relative ability of the silicon atom to transmit the inductive effect of the substituents to the indicator centre, can both decrease and increase after the introduction of different substituents. However, for highly electronegative substituents (RO, Cl), capable of effective $p_\pi-d_\pi$ conjugation with the silicon atom, the values of ρ^* for the compounds $R_{3-n}X_nSiY$ are as a rule smaller than for R_3SiX and tend to decrease further with increase of n (Nos.2–4 and 13–15 in Table 2, and 2, 6, 9, and 25–30 in Table 3). It has been suggested[45] that the decrease of the sensitivity of the indicator centre to the influence of the inductive effect of substituents with increase of the number of substituents X in the molecule is caused by the increase of the degree of $p_\pi-d_\pi$ bonding under these conditions.

* * *

Thus the results of the application of the Taft relations in order to establish correlations between the properties of organosilicon compounds and their structure demonstrates the applicability of the usual inductive (for alkyl and substituted alkyl groups) and steric constants of the substituents. In contrast to organophosphorus compounds,

substituted alkyl groups at the silicon atom do not exhibit a resonance effect with the exception of individual instances in α-substituted derivatives. The role of the hyperconjugation effect in silicon compounds has been only slightly investigated. The most specific feature of organosilicon compounds is p_π–d_π conjugation, the extent of which cannot in general be estimated with the aid of procedures usually employed in the calculation of resonance contributions. A preliminary estimate of the transmission coefficient of the silicon atom and silicon-containing groups showed that their ability to transmit the inductive effect of substituents is reduced compared with carbon (and germanium).

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Organic Syntheses Based on Carbon Dioxide

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Organic syntheses based on carbon dioxide are examined. Together with syntheses of organic compounds, certain aspects of the mechanism of the coordination of CO_2 to transition metal complexes are considered. The review includes studies published up to 1977.
The bibliography includes 171 references.

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I. INTRODUCTION

The use of carbon dioxide as the starting material for organic syntheses constitutes one of the most important problems of modern organic chemistry. There has been a recent growth of interest in the chemistry of carbon dioxide, the reserves of which in nature are practically inexhaustible. The most promising of the natural sources of carbon dioxide are coal and carbonates. The interest in the chemistry of carbon dioxide is to a large extent associated with the latest advances in metal complex catalysis, which permits the activation of the CO_2 molecule. The advances in this field permit the hope for a successful achievement of catalytic syntheses on the basis of CO_2.

In recent years there has been a sharp increase of the amount of CO_2 released into the atmosphere by engines, industry, and electric power stations. The average increase of the CO_2 content in the Earth's atmosphere as a result of the combustion of fuels is 0.2% per annum, which is extremely undesirable from the ecological point of view[1].

In view of the rapid depletion of the reserves of petroleum and the development of coal-chemical industries, the synthesis of compounds of practical importance based on CO_2 has also become important. On the basis of carbon dioxide derived from coal, it is possible to synthesise products which are nowadays manufactured using petroleum as the raw material; this makes it timely to develop effective methods for the synthesis of important organic compounds from CO_2.

This review deals with the principal literature data published in 1971–1977 and concerning the syntheses of organic compounds with participation of CO_2 (electrochemical and photochemical processes are not included).

II. SOME ASPECTS OF THE MECHANISM OF THE FIXATION OF CO_2 BY TRANSITION METAL COMPLEXES

1. Coordination to Transition Metal Complexes

Carbon dioxide is the highest oxide of carbon, which is much more reactive than nitrogen. The CO_2 molecule has a linear structure with an ionisation potential of 13.7 eV and an electron affinity of 3.8 eV.

The bond between CO_2 and the metal in complexes can be formed in principle via the following mechanisms:

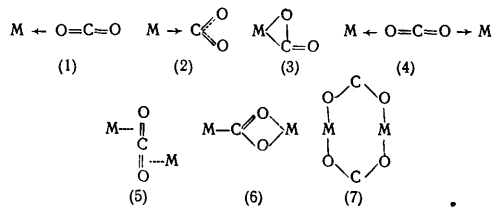


Table 1. Parameters of the infrared spectra of transition metal complexes of CO_2.

Complex	ν_{CO_2}, cm^{-1}	References
$Rh_2(CO_2)(CO)_2(PPh_3)_3$	1498,1368,813	2,3
$Rh_2Cl_2(CO_2)(PPh_3)_5$	1630	4,5
$Rh_2(CO_2)_2(CO)_2(PPh_3)_3C_6H_5$	1600,1355,800	3
$Rh(OH)(CO_2)(CO)(PPh_3)_2$	1602,1351,821	6
$RuH(OMe)(CO_2)(PPh_3)_3$	—	5,7
$Co(CO_2)(PPh_3)_3$	—	8
$Ni_2(CO_2)(PPh_3)_4$	1735	9
$Ni(CO_2)(PPh_3)_2$	1740,1698,1150	10
$Pt(CO_2)(PPh_3)_2$	1640,1370,1320	4
$C_6H_5AgCO_2Ag$	1496,1326,828	11
Cu(II)-ephedrine-CO_2	2350,2380	12
$Cu(OOCMe)(CO_2)(PPh_3)_2$	2620,1600,1302	13
$Cu(OOCMe)(CO_2)(PPh_3)_2$	821,1610,1420,1380, 830,650	14
$Ir(OH)(CO_2)(CO)(PPh_3)_2$	1636,1310,815	6
$Mo(CO_2)_2(PMe_2Ph)_4$	1760,1510,1335	15
$Cu_2(CO_2)(PPh_3)_4$	1475,1330,835	16

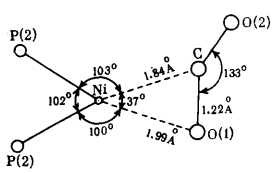
Evidently CO_2 interacts with the metal as an electron acceptor or as a powerful nucleophile via the carbon atom. The M–O bond formed via schemes (1) and (4) is less likely; the bond is most probably formed either via the carbon atom with transfer to the latter of electrons from the metal and the formation of organometallic compounds—derivatives of metal-carboxylates [scheme (2)]—or via a mechanism involving the formation of a π-complex with participation of the C=O double bond [schemes (5), (6), and (7)]. There are at present no data confirming unambiguously a particular structure. Some information is provided by the infrared spectra of transition metal complexes of CO_2, which are presented in Table 1. With

the exception of the complex $Rh_2(CO_2)(CO)(PPh_3)_3$, synthesised by oxidising with oxygen the compound $Rh_2(CO)_4(PPh_3)_3$, and also $Cu(CO_3)(PPh_3)_4$, all the complexes presented in Table 1 have been obtained by the direct interaction of the metal compounds with CO_2.

The presence of CO_2 in the rhodium complex obtained by passing CO_2 into a solution of triphenylphosphinerhodium chloride and containing one CO_2 molecule for two rhodium atoms has been confirmed by the isolation of carbon dioxide on heating, on reduction with $LiAlH_4$ with formation of methanol, and on quantitative substitution of CO_2 by carbon monoxide[17,18]. The alkylation reaction was used to detect the metal–carbon bond in this complex. If the complex contains only the metal–oxygen bond, alkylation should lead to the formation of a carbonate ester. On the other hand, if the complex is constructed in such a way that it contains a CO_2 fragment linked to the metal via the carbon atom, alkylation may be expected to lead to the formation of a derivative of an alkanecarboxylic acid. It was found that, when the rhodium complex is acted upon by methyl iodide, methyl acetate is formed. These data are satisfactorily consistent with structure (6) containing the fragment Rh–COO–Rh.

Pure gaseous carbon dioxide gives rise to two characteristic absorption bands in the infrared spectrum in the region of 2349 and 667 cm^{-1}. The appearance of three new absorption bands in the spectrum of the complex $Rh_2(CO_2)(CO)_2 \cdot (PPh_3)_3$ in the region of 1498, 1368, and 813 cm^{-1} is treated as a result of the coordination of CO_2 to the central metal atom and of the simultaneous formation of a bent configuration of the CO_2 molecule of type (II) and (III). Such a complex has also been obtained by the interaction of $Rh_2(CO)_4 \cdot (PPh_3)_4$ with $^{18}O_2$.[2] A polynuclear complex containing CO_2 gives rise to a single absorption band in the region of 1735 cm^{-1}, corresponding to the CO_2 group. This group is capable of coordinating with two nickel atoms with formation of a π-bond in a type (5) structure[9]. However, structure (6) has been attributed to the polynuclear rhodium complex of CO_2, which has a characteristic absorption band in the region of 1630 cm^{-1}; on interaction with methyl iodide, it gives rise to methyl acetate[4].

X-Ray diffraction analysis of the complex $Ni(CO_2)(PPh_3)_2$ confirmed the planar structure corresponding to the type (3) bond with the bent configuration of the CO_2 coordinated to the nickel atom[10]:



These data concerning the formation and properties of transition metal complexes containing CO_2 lead to ways of seeking new synthetic and catalytic reactions. The presence of CO_2 in the complexes as a ligand can be inferred from the evolution of CO_2 on heating the complexes or on treating them with acids and also from the displacement of CO_2 by carbon monoxide. The complex $Pt(CO_2)(PPh_3)_2$ has been obtained[4] from $Pt(PPh_3)_3$ and CO_2. In the presence of oxygen this reaction proceeds with formation of a platinum carbonate complex[19]:

$$Pt(PPh_3)_3 + O_2 + CO_2 \rightarrow Pt(CO_3)(PPh_3)_2 + PhPO \ .$$

Subsequently the platinum carbonate complex was obtained[19] by the reaction of $PtO_2(PPh_3)_2$, synthesised beforehand, with CO_2; in this case the CO_2 molecule is inserted in the metal–oxygen bond. The fixation of CO_2 in the complex $Mo(C_2H_4) \cdot (dpe)_2$ (where dpe = $Ph_2PCH_2CH_2PPh_2$) was achieved at room temperature[20] under the influence of u.v. radiation with formation of the molybdenum complex *cis*-$Mo(CO_2)(dpe)_2$ in boiling toluene. The authors explained the formation of the molybdenum carbonyl complex by the rupture of one C–O bond with the simultaneous oxidation of diphenylethane. The complex $Mo(CO_2)_2(PMe_2Ph)_2$ is unstable and, when an attempt is made to recrystallise it from tetrahydrofuran (THF), it is readily converted into the dinuclear complex $(PMe_2Ph)_3(CO) \cdot Mo(CO_3)_2Mo(CO)(PMe_2Ph)_3$. It has been suggested[15] that CO_2 is then reduced to CO_3^{2-} via the mechanism

$$2CO_2 + 2e \rightarrow CO_3^{2-} \ .$$

The analogous reactions involving the formation of carbonyl complexes from CO_2 and transition metal complexes have been described[20–23]. The following four most characteristic types of reaction can be distinguished among them:

$$(C_5H_5)(PPh_3)NiBr + Mg \rightarrow (C_5H_5)(PPh_3)NiMgBr \xrightarrow[MgBr_2]{CO_2} [(C_5H_5)(PPh_3)NiCOOMgBr] \rightarrow$$
$$\rightarrow [(C_5H_5)(PPh_3)NiCOOMgBr] \rightarrow [(C_5H_5)(PPh_3)NiCO^+] \rightarrow (PPh_3)_2Ni(CO)_2 \ ;$$

$$(C_5H_5)_2MoH_2 + AlMe_3 \rightarrow [Mo_2{-}Al_3 \text{ polynuclear complex }] \xrightarrow{CO_2+H_2O} [(C_5H_5)_2Mo(CO)Br]^+ \ ;$$

$$RhCl(PPh_3)_3 + CO_2 \xrightarrow{HSi(OEt)_3} [RhH\{Si(OEt)_3\}Cl(PPh_3)_2] \rightarrow RhCl(CO)(PPh_3)_2 \ ;$$

$$RuCl_2(PPh_3)_3 + CO_2 \xrightarrow{HSi(OEt)_3} RuCl_2(CO_2)(PPh_3)_2 \ .$$

The opposite case, involving the interaction of CO_2 with the triphenylphosphine complex of copper and formation of the copper carbonate complex, has also been described in the literature[16]:

$$iso\text{-}BuCu(PPh_3)_2 + 2CO_2 \xrightarrow[0.5\ h;\ -40\ ^\circ C]{THF}$$
$$iso\text{-}BuCCu(CO_2)(PPh_3)_2 \xrightarrow[6\ h;\ 0\ ^\circ C]{CO_2} Cu_2(CO_3)(PPh_3)_4 \ .$$
$$\|O$$

The reaction proceeds via a stage in which an acyl complex is formed and, when carbon dioxide is passed into its solution for a long time, is converted into a crystalline copper carbonate complex. When this complex interacts with hydrochloric or sulphuric acid solutions, CO_2 is evolved in molar proportions of 1 : 2 in relation to copper.

2. CO_2 Insertion Reactions

In order to synthesise various organic compounds, it is necessary that the carbon dioxide activated by coordination to transition metal complexes should form a new substrate via insertion in the M–H, M–C, M–O, or M–N bonds. Such insertion can be regarded as nucleophilic attack on the carbon atom in the CO_2 molecule which proceeds via two possible pathways:

(1) normal insertion with formation of the M–O bond and the formate:

$$M^{\delta+}-L^{\delta-} + O^{\delta-}\equiv C^{\delta+}=O \rightarrow M-O-\overset{O}{\overset{\|}{C}}-L \ ;$$

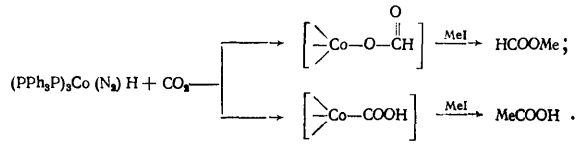
(2) anomalous insertion with formation of compounds with a metal–carbon bond—metal-carboxylates:

$$M^{\delta-}-L^{\delta+} + O^{\delta-}\equiv C^{\delta+}=\dot{O} \rightarrow M-\overset{O}{\overset{\|}{C}}-O-L;$$
$$L=H,\ C,\ O,\ N \quad etc.$$

The anomalous insertion of CO_2 in the M–L bond is encountered extremely rarely.

Reactions involving insertion in the M–H and M–C bonds have been examined in detail in another review[17] and we shall therefore deal with them extremely briefly.

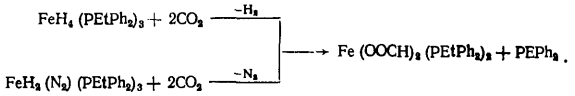
(a) *The insertion of CO_2 in the M–H bond.* The reaction of CO_2 with a nitrogen-containing cobalt hydride complex and subsequent methylation of the reaction products by methyl iodide lead to both methyl formate—the product of the normal insertion of CO_2 in the M–H bond[24,25]—and to acetic acid and methyl acetate—the products of the anomalous insertion of CO_2:[18]



The reaction proceeds via a stage in which a cobalt formate complex is formed, which also happens when CO_2 interacts with $CoH_3(PPh_3)_3$.

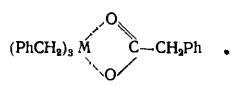
On interaction with CO_2 at room temperature, ruthenium and rhodium hydride complexes[26–28] give rise to a formate complex with a single hydride atom, in contrast to the formate complex, formed on pyrolysis or on interaction with PPh_3, N_2, H_2, CO, CS_2, HHal, and RHal, which readily splits off CO_2.

Iron hydride complexes in the crystalline state or in solution readily interact with CO_2 under the influence of light to form an iron diformate complex[29]:



In contrast to the insertion of CO_2 in the Ru–H bond, this reaction is irreversible; when the resulting complex interacts with methyl iodide, ethyl formate is formed.

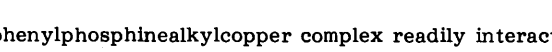
(b) *The insertion of CO_2 in the M–C bond.* Various organic compounds with functional groups can be obtained by the insertion of CO_2 in the M–C bond. Organometallic complexes having the general formula $M(CH_2Ph)_4$ (where M = Ti or Zn) effectively absorb CO_2 in solution in the molar proportions 1 : 2 and subsequent hydrolysis of the resulting substrate leads to the formation of phenylacetic acid and triphenylmethanol[30], which indicates a normal mechanism of the insertion of CO_2 in the M–C bond with formation of a cyclic complex:



Similarly, the interaction of dimethyltitanocene with CO_2 results in the formation of a stable titanocenium acetate, the reaction of which with methanol yields methyl acetate[31]. The formation of the above cyclic metal-containing structure has been confirmed spectroscopically[32].

The reaction of CO_2 with an organometallic cobalt compound containing the ethyl group proceeds via both pathways with formation of cobalt propionate (normal insertion) and a metal-carboxylate ester (anomalous insertion) as insertion products[18,33]. A carboxylate complex of cobalt is formed when propionic acid acts on the complex $LCO(CO_3)COOEt$. When the carbonate complex is treated with methyl iodide, methyl propionate and a small amount of methyl formate are formed[18].

The intermediate complex containing the COOEt group [ν(CO) = 1713 cm^{-1}] is formed from the iridium[34], cobalt[35], ruthenium, and osmium complexes in the presence of alcohol and carbon monoxide[36]. The insertion of CO_2 in the Rh–C bond in a phenylrhodium complex proceeds via the normal pathway[37]:

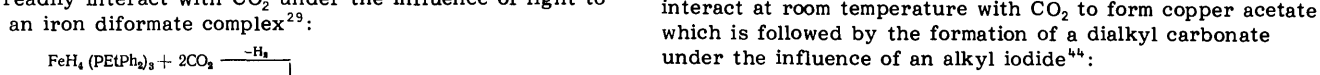


A triphenylphosphinealkylcopper complex readily interacts with CO_2 at room temperature via the anomalous insertion pathway (involving the Cu–C bond) to form unstable metal carboxylate complexes and copper carbonates[13,14,38]:



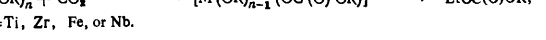
The initial alkyl complex of copper is used as the catalyst in the synthesis of nitroalkanecarboxylic acid from CO_2 and a nitroalkane[38]. The reaction with the cyanomethyl complex of copper proceeds via the normal pathway involving the insertion of CO_2 in the Cu–C bond with formation of a copper cyanoacetate complex[39], which can be used to synthesise carboxylic acids from acetylenic hydrocarbons at atmospheric pressure[40]. There are data concerning the insertion of carbon dioxide in benzyl–titanium or benzyl–zirconium[41], methyl–titanium[7,42], and Pd–C [43] bonds.

(2) *The insertion of CO_2 in the M–O bond.* Transition metal alkoxides and hydroxides interact with CO_2 via insertion in the M–O bond (normal insertion). Copper alkoxides interact at room temperature with CO_2 to form copper acetate, which is followed by the formation of a dialkyl carbonate under the influence of an alkyl iodide[44]:

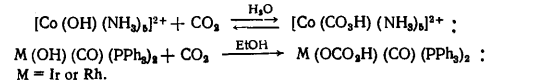


The presence of absorption bands in the region of 1665 and 1305 cm^{-1} in the infrared spectrum of the copper acetate complex and the formation of an asymmetric dialkyl carbonate on interaction with RI confirm the normal insertion of CO_2 in the Cu–O bond[44]. In benzene solution the analogous copper compound reacts with CO_2 to form an alkyl carbonate complex[45]:

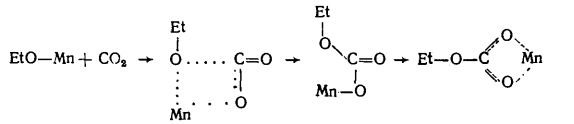
The normal insertion of CO_2 in the M–C bonds is observed also for $Ti(OBu)_4$, $Zr(OBu)_4$, $Fe(OEt)_3$, $Nb(OEt)_3$, and $Zr(OEt)_4$.[46] All these reactions proceed via the mechanism



The reactions with zinc[47], mercury[48], and tin[49,50] compounds proceed via an analogous mechanism involving the insertion of CO_2 in the M–O bond. The hydroxo-complexes of cobalt and other transition metals also react with insertion of CO_2 in the M–O bond and the formation of carbonate complexes[51,52]:



The reaction with the hydroxocobalt complex proceeds in an aqueous medium and the reactions with the hydroxo-complexes of iridium and rhodium take place in alcohol. In the presence of alcohol *in vacuo* alkoxomanganese reacts with CO_2 in the vapour phase to form a complex with an Mn–O bond[53]:



(d) *The insertion of CO_2 in the M–N bond.* Reactions involving the insertion of CO_2 in the M–N bond also proceed via the normal pathway in accordance with the mechanism[54–60]

$$M(NMe_2)_n + n\,CO_2 \rightarrow M(O_2CNMe_2)_n;$$
$$M = Ti, Zr, V, \text{or } Mo\ (n=4);\ Nb \text{ or } Ta\ (n=5);\ Mo \text{ or } W\ (n=3).$$

The group $\rangle C{=}O$, of a metal carbamate complex, readily exchanges for $^{13}CO_2$, forming a labelled compound detectable by NMR:[58]

$$ML_n^* + x^{12}CO_2 \rightleftarrows ML_mL^*_{n-m} + m^{12}CO_2 + (x-m)^{13}CO_2;$$
$$L = O_2^{12}CNMe;\ L^* = O_2^{13}CNMe.$$

The activation energy for the exchange reaction of the zirconium complex is 44 ± 8 kJ mol^{-1} and that for the tungsten complex is about 96 kJ mol^{-1}. When the *N,N'*-ethylenebis-(salicylideneiminato)cobalt(II) complex is reduced with sodium, the product is a mixed $NaCo^I$ complex, which readily reacts with CO_2 to form Co–C(O)–ONa.[61] The use of the latter as the catalyst can lead to new possibilities for the synthesis of different functional compounds. Aluminium[62], boron[63], silicon[64], germanium[6], tin[65,68], phosphorus[65], arsenic[67], and zinc[69] amide compounds also react with CO_2, forming carbamide complexes (via the normal insertion pathway).

III. THE REACTIONS OF CO_2 WITH ORGANIC COMPOUNDS

1. The Addition of CO_2 to Carbanions

It is known that, when organomagnesium compounds are acted upon by CO_2, carboxylic acids are formed[70]:

$$RMgX + CO_2 \rightarrow RCOOMgX \xrightarrow{H_2O} RCOOH.$$

However, the reaction of CO_2 with dimethoxymagnesium proceeds with formation of methanol[73]:

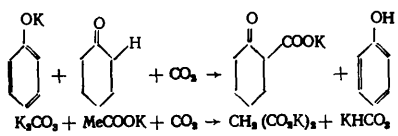
$$Mg(OMe)_2 + NO_2Me + CO_2 \rightarrow NO_2CHCOOMg + 2MeOH$$

or

$$Mg(OMe)_2 + CO_2 \rightleftarrows MeOMgOCOOMe;$$
$$MeOMgOCOOMe + NO_2Me \rightleftarrows NO_2CHMg + 2MeOH.$$

Ethylene and propene react with CO_2 in the presence of EtMgBr [71] and $Sn(OCH_2CH_2NMe_2)_2$ to form ethylene and propylene carbonates respectively in quantitative yields at 100 °C and a CO_2 pressure of 5–9 atm.

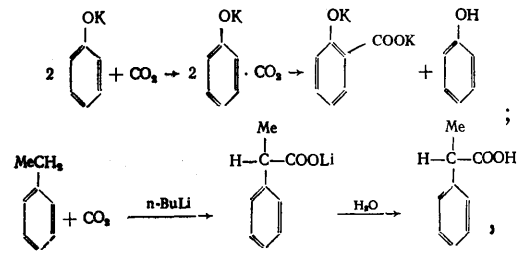
The carboxylation of cyclohexanone[74] and an acetate salt[75] proceeds differently—via the substitution of mobile hydrogen atoms in the molecule:



$$K_2CO_3 + MeCOOK + CO_2 \rightarrow CH_2(CO_2K)_2 + KHCO_3.$$

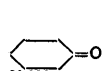
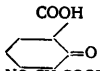
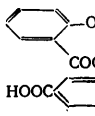
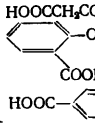
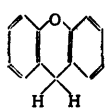
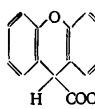
Table 2 presents data for the carboxylation of various organic compounds with a mobile hydrogen atom in the α-position in the presence of potassium carbonate and THF.[76] The data presented show that the yields of the reaction products per unit time depend on the basicity of the initial reactant.

The Kolbe–Schmidt reaction, occurring as a consequence of π-electron transfer from the aromatic ring to CO_2,[77] which has found industrial applications, and the carboxylation of ethylbenzene[78],



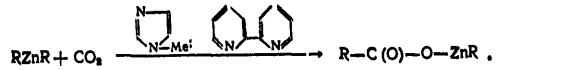
constitute prototypes of the reactions presented above. They can be regarded as nucleophilic interaction of a carbanion, with a characteristic relation between the reactivity and electronegativity of the initial reactants.

Table 2. Carboxylation of organic compounds in the presence of K_2CO_3.[76]

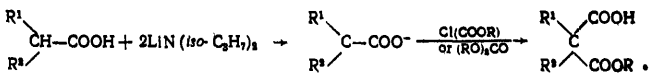
Initial reactant	pK_a	t, °C	p_{CO_2}, atm	τ, h	Reaction products	Yield, %
	<15	room	1	2		40
$MeNO_2$	11	room	1	2	NO_2CH_2COOH	25
$EtNO_2$	9	room	1	2	$NO_2C(COOH)HMe$	15
$PrNO_2$	—	room	1	2	$NO_2C(COOH)HEt$	10
$MeC(NO_2)HMe$	9	room	1	2	$MeC(COOH)(NO_2)Me$	0
MeCN	25	70	2	45	$CNCH_2COOH$	1
	—	70	2	—		0.3 0.3
MeCOMe	20	room	1	11	$MeCOCH_2COOH$ $HOOCCH_2COCH_2COOH$	7 7
MeCOOMe	24	70	2	72	$HOOCCH_2COOMe$ 	10 1 1
	29	95	1	4		10 20
MeCOCOOMe	0	—	1	1	$(CH_2COCOOMe)_2$ $C(COOH)H_2COCOOMe$	33 15

According to Pauling's data[1], alkyl derivatives of metals (R_xM) with an electronegativity less than 1.5 interact with carbon dioxide, but when the electronegativity is greater than 1.5, they do not react. Thus trialkylaluminium (the electronegativity of aluminium is 1.5) readily interacts with CO_2, while dialkylzinc (the electronegativity of zinc is 1.6)

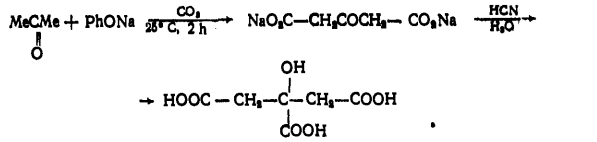
does not react with CO_2 at room temperature at atmospheric temperature[79,80]. Only the introduction of tertiary amines of the type of methylimidazole or pyridine into the reaction medium increases the reactivity of the initial reactant[81]:



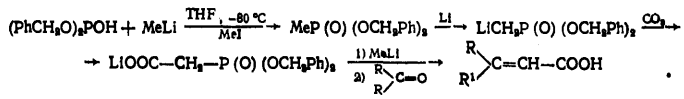
The synthesis of acids with the iso-structure, which are derivatives of malonic acid (yield 46–80%), proceeds via a carbanionic mechanism[82]:



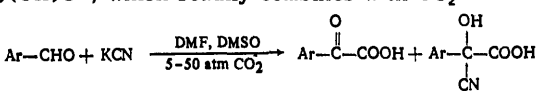
Citric acid has been obtained from acetone and CO_2 in solution in diglyme[83]:



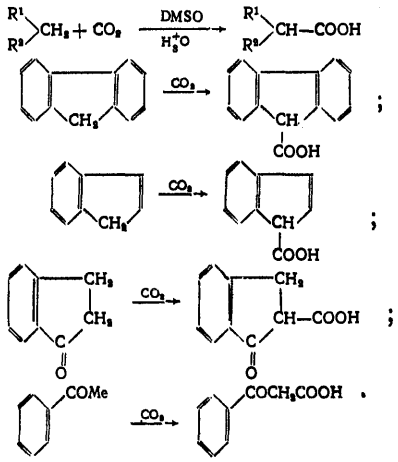
Butadiene reacts with CO_2 in a solution of sodium phenoxide in dimethylformamide (DMF) at 50 °C with formation of muconic acid (yield 81%).[84] By analogy with the Wittig–Horner vinylcarboxylation reaction, α,β-unsaturated carboxylic acids have been obtained from dibenzyl phosphate and CO_2 in the presence of Me_3Li and MeI at −80 °C:[85]



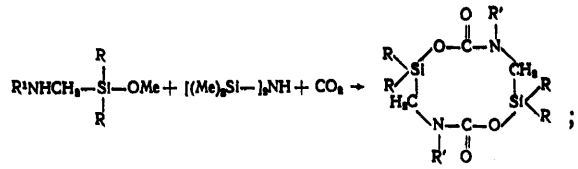
When an aldehyde reacts with potassium cyanide in DMF or dimethyl sulphoxide (DMSO), the product is the carbanion $R(CN)(OH)C^-$, which readily combines with CO_2:[86]



The possibility of synthesising carboxylic acids and their derivatives in yields of 30–80% by the carboxylation of a ketone and hydrocarbons with a mobile hydrogen atom had been demonstrated[86,87]:

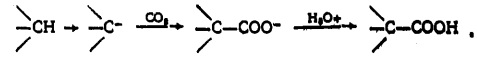


The carboxylation of organosilicon compounds proceeds via a carbanionic mechanism[88]:



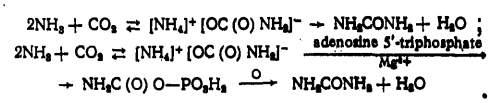
R=Me; MeO; R'=H, CH_2=$CHCH_2^-$, Me_2CH–CH_2^-, or n-Bu.

Organic compounds with a weak acidity and tending to be metallated with subsequent formation of a carbanion enter into the above reactions; the nucleophilic attack by this carbanion on CO_2 leads to the formation of carboxylic acids or their derivatives via the mechanism



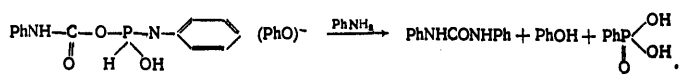
2. Reactions of CO_2 with Nitrogen-Containing Compounds

Urea, which is of practical importance, is obtained by the reaction of carbon dioxide with ammonia at 200–300 °C under pressure[89–91]:



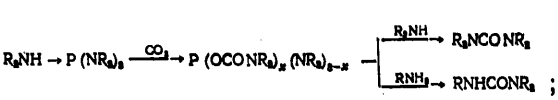
We may note that in the living organism urea is continuously biosynthesised, leading to the fixation of ammonia, which is harmful to the organism.

The synthesis of urea derivatives from an amine and CO_2 at atmospheric pressure in a quantitative yield was achieved for the first time by Yamazaki[92]. When CO_2 was passed into a solution of $(PhO)_2POH$ and $PhNH_2$ in pyridine for 4 h (at 40 °C), *N,N'*-diphenylurea was formed in 85% yield, while in THF the yield was 93%:



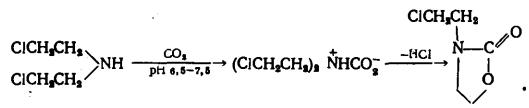
When carbon dioxide is replaced in this reaction by carbon disulphide, the product is PhNHCSNHPh (yiled 100%). These reactions can be used to synthesise polyureas or polythioureas[93].

Primary or secondary amines react with CO_2 in the presence of PCl_3 and pyridine at 60 °C with formation of symmetrical disubstituted ureas[94]:



Under analogous conditions, aromatic amines react with CO_2 in the presence of $PhOPCl_2$ in pyridine to form polyureas[95].

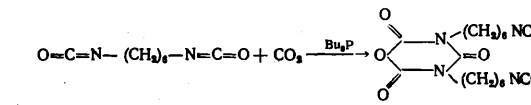
3-(2-Chloroethyl)-2-oxazolidinone has been obtained from CO_2 and di(2-chloroethyl)amine in the presence of 0.6 mole of sodium bicarbonate at 31 °C:[96,97]



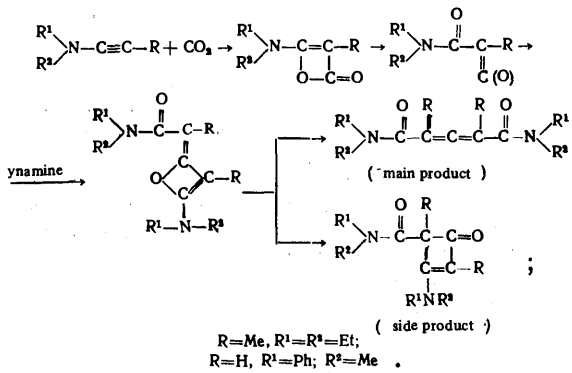
Dialkyl-substituted formaldehydes have been obtained from primary and secondary amines, CO_2, and H_2 at pressures up to 30 atm in the presence of phosphine complexes of ruthenium of the type $(PPh_3)_4RuH_2$, $(PPh_3)_4RuCl_2$, $Ph_2PCH_2CH_2PPh_2$–$RuCl_3$–EtAl, or $(PhO)_3P$–$RuCl_3$–EtAl at 130 °C (yield 60%).[98] The reaction can proceed catalytically in the presence of cobalt, rhodium, iridium, palladium, platinum, and copper complexes under analogous conditions[98]:

$$R_2NH + CO_2 + H_2 \rightarrow HC(O)NR_2 + H_2O\ .$$

In the presence of Bu_3P diisocyanates react with CO_2 to form oxadiazinone compounds[99]:



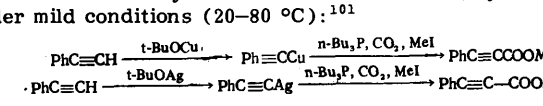
Unsaturated compounds with a high electron density of the type of ynamine readily react with CO_2 at 20 °C to form allenedicarboxamide derivatives in 100% yield[100]:



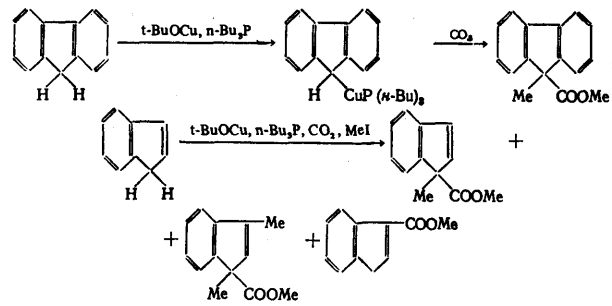
R=Me, R^1=R^2=Et;
R=H, R^1=Ph; R^2=Me .

3. Reactions of CO_2 with Unsaturated Hydrocarbons and Their Derivatives

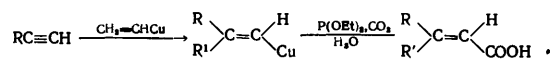
As already mentioned above, the insertion of CO_2 in the M–C bond can serve as the basis of the synthesis of various compounds with functional groups from unsaturated hydrocarbons and their derivatives. Thus the insertion of CO_2 in the Cu–C and Ag–C bonds, depending on the σ-donor ligand (whose presence is essential), constitutes the basis of the synthesis of carboxylic acids from unsaturated hydrocarbons under mild conditions (20–80 °C):[101]



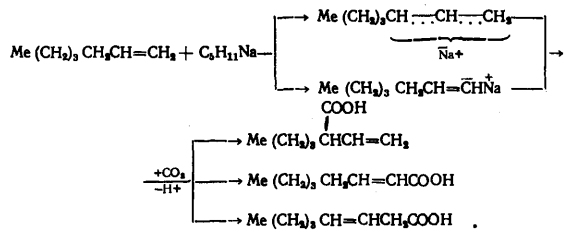
The yield of phenylacetylenecarboxylic acids from phenylacetylene and CO_2 in the presence of ligands of the type of n-Bu_3P and t-BuNC or t-BuOCu and t-BuOAg was 70%. Fluorene[101] and indene[45] are carboxylated under analogous conditions in the presence of methyl iodide with formation of methyl esters of methylfluorenecarboxylic and methyl- and dimethyl-indenecarboxylic acids respectively:



Methyl- and butyl-acetylenes react with CO_2 in the presence of vinylcopper and triethoxyphosphine $P(OEt)_3$ in hexamethylphosphoramide at −30 °C with formation of stereospecific β,β′-unsaturated carboxylic acids (yield 96%):[102]



When α-olefins are metallated by pentylsodium or alkyllithium in aprotic solvents at room temperature a hydrogen atom attached to a carbon atom in the allyl or vinyl position is substituted with formation of organometallic compounds. Carboxylation of the latter yields unsaturated acids[103,104]:



The reactivity of α-olefins in the metallation reaction is usually attributed to the ability of the hydrogen atom to be converted into a proton under the influence of bases of appropriate strength[103]. The use of complex-forming solvents in metallation reactions involving alkyl-lithium[105–109] as well as alkylmagnesium[110,111] leads to the coordination of the electron-donating groups of the solvent to the metal cation, which tends to increase the polarity of the metal–carbon bond. The most effective solvent in the metallation reaction proved to be triethylamine, in the presence of which the overall yield of carboxylic acids reached 97.7%.[112].

Indene, fluorene, acetophenone, and benzyl thioacetate are carboxylated at the active CH_2 group in triethylamine or triethylenediamine in the presence of $MgCl_2$ at p_{CO_2} = 5 atm at room temperature with a yield of the required product up to 80%.[113] Indene-3-carboxylic acid, fluorene-9-carboxylic acid, phenylacetic acid, and benzylthiocarboxylic acid were obtained from indene, fluorene, acetophenone, and benzyl thioacetate respectively. The reaction conditions were as follows: an equimolar amount of $MgCl_2$ in relation to the carboxylated reagent and duration of experiment from 17 to 72 h.

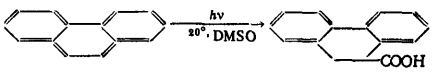
Diene hydrocarbons with conjugated double bonds (butadiene, isoprene, 2,3-dimethylbutadiene, and penta-1,3-diene) are readily carboxylated with formation of dicarboxylic acids under mild conditions with participation of an alkali metal phenoxide[114]. Thus at atmospheric pressure in THF and in the presence of an equimolar amount of sodium phenoxide, butadiene is carboxylated at 50 °C to muconic acid in 81% yield:

$$CH_2{=}CH-CH{=}CH_2 + 2CO_2 \xrightarrow[50^\circ C]{PhONa,\ THF} HOOC-CH{=}CH-CH{=}CH-COOH.$$

The reactions considered are characteristic of unsaturated hydrocarbons and their derivatives capable of forming an M–C bond in which CO_2 can be inserted via the anomalous pathway with formation of compounds of the metal-carboxylate type.

4. Reactions Involving the Addition of CO_2 to a Radical-Anion

It has been shown that CO_2 can readily add to a radical-anion with formation of a charge-transfer complex between a donor base and an acceptor. Thus, the carboxylation of phenanthrene in a solution of $PhN(CH_3)_2$ in DMSO at p_{CO_2} = 4 atm and room temperature under the influence of u.v. for 17 h yielded 9,10-dihydrophenanthrenecarboxylic acid (yield 41%):[115]



The reaction proceeds analogous with anthracene, naphthalene, pyrene, and biphenyl in a tertiary amine and dimethylaniline[1]. The mechanism of these reactions has been treated in terms of the intermediate formation of a charge-transfer complex under the influence of ultraviolet light between a strong electron donor (an amine) and aromatic hydrocarbons of the type $\overline{ArH}\cdot R_3\overset{+}{N}$. CO_2 then attacks the complex with formation of the radical-anion $(ArH)^{\cdot}-COO^-$, which readily combines with a hydride hydrogen atom from the solvent:

$$(ArH)\begin{matrix}H\\ \diagdown\\ COO^-\end{matrix} \rightarrow (ArH)\begin{matrix}H\\ \diagdown\\ COOH\end{matrix}.$$

In the presence of acetonitrile and p-NCC_4H_4NC, p-methoxystyrene gives rise, under the influence of ultraviolet light to a radical-cation, which interacts with CO_2.[116]

The free radicals formed in the homolytic dissociation of the C–C bond under the conditions of the cracking of alkanes proved to be extremely reactive in relation to CO_2. Thus the vapour-phase cracking of the higher C_{17}–C_{19} paraffins and C_{20}–C_{40} paraffin wax in CO_2 at 500–700 °C yielded a mixture of saturated carboxylic acids (contact time 0.1–10 s):[117]

$$R-CH_2-Me \rightarrow R^{\cdot} + \dot{C}H_2Me;$$
$$R^{\cdot} + CO_2 + RCH_2Me \rightarrow RCOOH + R\dot{C}HMe;$$
$$\dot{C}H_2Me + CO_2 + RCH_2Me \rightarrow MeCH_2COOH + R\dot{C}HMe.$$

5. Reactions Involving the Addition of CO_2 to Ylid Compounds of Phosphorus

Ylid compounds of phosphorus readily interact with CO_2 at room temperature and atmospheric pressure with formation of betaine compounds (A), capable of being converted into carboxylic acid on hydrolysis in an alkaline medium[118]:

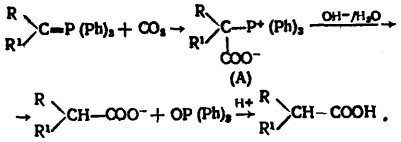
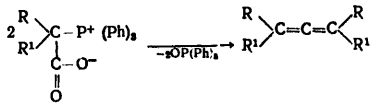


Table 3 presents data for the synthesis of carboxylic acids from various P-ylids and CO_2.

Allene has been obtained in yields up to 36% by the pyrolysis of such a betaine at 200 °C:[118]



It has been suggested[118] that the reaction proceeds via a stage in which a keten is formed. On subsequent decarboxylation, the allene is formed from two molecules. This hypothesis is confirmed by the mechanism of the synthesis of an isocyanate by the reaction of CO_2 with the dialkyl N-alkylphosphoramidate anion via a stage involving the formation of carbamate at room temperature[119]:

$$(EtO)_2P(O)-NHR \xrightarrow{OH^-} (EtO)_2P(O)-\overline{N}R \xrightarrow[25^\circ C]{CO_2} (EtO)_2P(O)-NR \rightarrow$$
$$\rightarrow (EtO)_2P(O)-O^- + R-N{=}C{=}O.$$

The yield of isocyanates is 73% for R = iso-C_4H_9, 80% for R = C_6H_{11}, and 88% for R = t-C_4H_9. We may note that the dialkyl N-alkylphosphoramidate anion reacts with carbon disulphide to form an isothiocyanate under analogous conditions[119].

Table 3. Carboxylation of P-ylids[118].

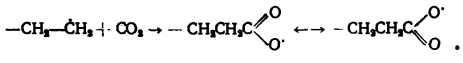
R	R¹	Yield of betaine (A), %	Yield of carboxylic acids, %
$-(CH_2)_2-$		94	90
$-(CH_2)_3-$		91	89
$-(CH_2)_5-$		98	86
$-(CH_2)_6-$		82	85
Me	Me	99	85
Ph	H	68	80

6. Organic Syntheses Based on CO_2 Under the Influence of Radiation

Alcohols, amines, carboxylic acids, and saturated and unsaturated hydrocarbons can be carboxylated with the aid of ionising radiation under the influence of free radicals, radical-ions, free atoms, and biradicals[120]. The chemical processes induced by the ionising radiation are analogous to photochemical reactions. However, whereas photochemical reactions proceed selectively, under the influence of ionising radiation the molecules are supplied with such a large amount of energy that they are involved in a wide variety of chemical processes, occurring simultaneously, which leads to a decrease of selectivity.

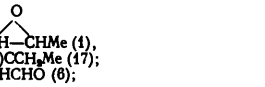
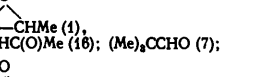
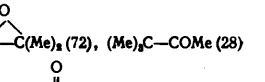
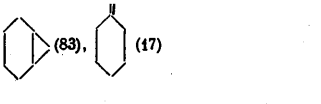
The yield of products (G) of the reaction occurring under the influence of radiation is usually calculated from the number of molecules formed following the absorption of 100 eV of energy. The reaction is performed in an aqueous solution of HCOOH or HCOONa. Thus, irradiation of a mixture of solid carbon dioxide and ethanol with γ-rays having an energy of 2 MeV yielded lactic acid ($G = 0.06$), while the use of cyclohexane, cyclohexene, and ethylamine instead of ethanol resulted in the formation of cyclohexanecarboxylic acid ($G = 0.07$),[120] a mixture of cyclohexenecarboxylic acids ($G = 0.11$), and α-alanine ($G = 0.17$).[121] Furthermore, acetic acid had been obtained from CH_4 and CO_2 by a gas-phase reaction. The replacement of CO_2 by formic acid does not affect the composition of the reaction products. Hummel and Barzynski[122] obtained carboxylic acids with a number of carbon atoms greater by unity than in the initial compound in yields of 0.15, 2.12, 2.16, 2.24, 0.33, and 0.37 by the reaction of CO_2 with cyclohexane, n-hexane, n-heptane, cyclo-octane, benzene, and toluene respectively under the influence of γ-radiation.

Ethylene reacts with CO_2 at 100 °C under the influence of γ-radiation with formation of a mixture of linear carboxylic acids having a molecular weight of 670.[123] It has been suggested that these acids are formed as a result of the addition of CO_2 to a polyethylene radical via a stabilised resonance radical, which is energetically unsuitable for further chain growth:



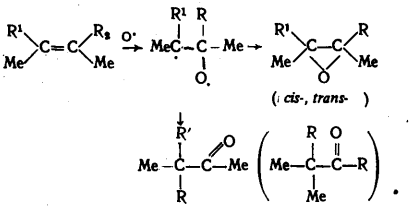
When an aqueous solution of CO_2 from which oxygen has been removed is γ-irradiated, formaldehyde and acetaldehyde are formed; the yields depend on the pH of the medium[124–126]. The addition of an insignificant amount of $FeSO_4$ (10^{-3} M) in an alkaline medium leads to a sharp increase of the yield of aldehydes. When the reaction is carried out in an acid medium, carboxylic acids are formed preferentially: HCOOH, $(COOH)_2$, CHOCOOH, and glyoxal[127].

Table 4. Radiolysis of olefins and CO_2 at room temperature.

Olefin	Relative velocity k_1/k_2	Reaction products (yield, %)
cis- Me—CH=CH—Me	1.0	 Me—CH—CHMe (1), MeC(O)CH$_2$Me (17); (Me)$_2$CHCHO (6);
$(Me)_2C$=CHMe	1.3	 $(Me)_2$C—CHMe (1), $(Me)_2$CHC(O)Me (16); $(Me)_2$CCHO (7);
$(Me)_2C$=C$(Me)_2$	1.7	 $(Me)_2$C—C$(Me)_2$ (72), $(Me)_2$C—COMe (28)
	1.3	 (83), (17)

Alicyclic and cyclic olefins mixed with H_2CO_3 in a steel autoclave (molar ratio olefin : CO_2 = 1 : 100) are converted into epoxy- and carbonyl compounds at room temperature or at 0 °C under the influence of γ-radiation (see Tables 4 and 5).

The formation of *cis*- and *trans*-2,3-epoxybutanes is treated as a result of stereoisomeric transformations of the adduct resulting from the radical addition of an oxygen atom to *cis*-but-2-ene:



The data in Table 5 show that the reactions of aromatic olefins proceed with formation of a mixture of epoxy- and carbonyl compounds with the exception of 1,1-diphenylethylene, which does not form epoxy-compounds but is converted into carbonyl compounds and oligomers (degree of conversion 97%).

Table 5. Radiolysis of aromatic olefins and CO_2 at 0 °C.

Olefin	Conversion, %	Reaction products (yield, %)
Ph—CH=CH$_2$	—	 PhCHO (4), PhCH—CH$_2$ (74) PhCH$_2$CHO (22)
PhC(Me)=CH$_2$	—	 PhC(O)Me (35), PhC(Me)—CH$_2$ (31), PhC(Me)HCHO (34)
cis- PhCH=CHPh	75	 PhCHO (21), PhCH—CHPh (*cis*-21, *trans*-53), (Ph)$_2$CHCHO (3), PhCH=CHPh (*trans*-2)
trans- PhCH=CHPh	52	 PhCHO (37), PhCH—CHPh (*cis*-1, *trans*-56) (Ph)$_2$CHCHO (2), PhCH=CHPh (*cis*-4)
$(Ph)_2C$=CH$_2$	97	PhC(O)Ph (13), (Ph$_2$)CHCHO (13), oligomer (74)

Under a CO_2 pressure up to 1 atm or in the presence of an equimolar amount of Na_2CO_3, ethanol gives rise to lactic acid under the influence of γ-radiation,[129,130] whose yields depend on the pH of the medium. $G = 1$ in an acid medium and reaches 2 in an alkaline medium. At pH 4–6 methanol reacts with CO_2 to form glycolic acid with $G = 1$–2.3.[130,131] The reaction proceeds via the mechanism

$$H_2O \rightarrow e^-_{aq},\ H_3O^+,\ H^+,\ OH^-,\ H_2,\ H_2O_2$$
$$MeOH + H^+ \text{ (or; } OH^-) \rightarrow \dot{C}H_2OH + H_2 \text{ (or } H_2O)$$
$$CO_2 + H^+ \rightarrow COOH \quad (k \leqslant 8 \cdot 10^6 \text{ mol}^{-1}\text{ s}^{-1}),$$
$$CO_2 + e^-_{aq} \rightarrow CO_2^- + n\,H_2O \quad (k = 7.67 \cdot 10^9 \text{ mol}^{-1}\text{ s}^{-1});$$
$$\dot{C}H_2OH + COOH \rightarrow CH_2(OH)\,COOH;$$
$$\dot{C}H_2OH + CO_2 \rightarrow CH_2(OH)\,COO^-;$$
$$CH_2(OH)\,COO^- + H_3O^+ \rightarrow CH_2(OH)\,COOH + H_2O.$$

In order to suppress the formation of CO_2^-, the reaction is carried out with methanol freed from oxygen.

The radiation-induced carboxylation of aliphatic amines under conditions analogous to those in the carboxylation of

alcohols, gives rise to aminoacids[132,133]. Thus, when a solution of methylamine saturated with CO_2 is irradiated with γ-rays, glycine is formed with a yield $G = 0.8$ at pH 9:

$$MeNH_2 + H^+ \rightarrow \dot{C}H_2NH_2 + H_2;$$
$$MeNH_2 + OH^- \rightarrow \dot{C}H_2NH_2 + H_2O;$$
$$\dot{C}H_2NH_2 + CO_2 \rightarrow CH_2NH_2COO^-;$$
$$\dot{C}H_2NH_2 + \dot{C}OOH \rightarrow CH_2NH_2COOH;$$
$$CH_2NH_2COO^- + H_3O^+ \rightarrow CH_2NH_2COOH + H_2O.$$

At pH > 9 the yield of glycine falls sharply, owing to the decrease of the amount of CO_2 and the occurrence of side reactions. An analogous behaviour has been observed also in the carboxylation of ethylamine[133].

The radiation-induced carboxylation of formic acid with the aid of $^{14}CO_2$ at pH 3.5 leads to the formation of labelled oxalic acid ($^{14}COOH.COOH$) with $G = 1.2$.[129,130] An increase of the pH of the medium from 5 to 6 leads to an increase of the yield of oxalic acid to $G = 7.2$ and $G = 7.6$ respectively[134,135]:

$$CO_2^- + HCOO^- \rightarrow (CO_2^- \cdot HCOO^-);$$
$$(CO_2^- \cdot HCOO^-) + CO_2 \rightarrow CO_2^- + (COO \cdot COOH^-).$$

In neutral and alkaline media the reaction proceeds with the preferential formation of oxalic acid, which is suppressed in an acid medium as a consequence of the reaction $COOH \rightarrow HCOO$.[136]

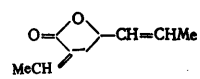
The effect of γ-radiation on aromatic hydrocarbons of the type of benzene, toluene, and xylene in a mixture with CO_2 at 0 °C leads to the formation of substituted phenols[137]. Since the addition of SF_6, which is a powerful electron acceptor, in the reaction between CO_2 and toluene did not result in the formation of cresol and only lines corresponding to O^- and CO_3^- were noted in the mass-spectrum of CO_2, the following reaction mechanisms were proposed:

$$MePh \rightarrow MePh + e;$$
$$CO_2 \rightarrow CO_2^+ + e \text{ (were } CO + O);$$
$$O + e \rightarrow O^-;$$
$$MePh + O^- \rightarrow MePhO^-;$$
$$O^- + CO_2 \rightarrow CO_3^-;$$
$$MePh + CO_3^- \rightarrow MePhO^- + CO_2;$$
$$MePhO^- + M^+ \rightarrow MePhOH + M.$$

7. Catalytic Syntheses Based on CO_2

Catalytic reactions based on CO_2 constitute a relatively little investigated field of organic chemistry. It was noted above that the insertion of CO_2 in molecules of complex compounds can serve as a basis of catalytic processes designed to obtain different functional compounds. Thus the reaction of a cobalt carboxylate complex containing an ethyl group with MeI or H^+ yields respectively ethyl acetate or ethyl formate[18,33]. The anomalous pathway in the insertion of CO_2 in the M–L bond with formation of compounds containing a metal–carbon bond (metal-carboxylic acids) suggests the possibility of the synthesis of unsaturated carboxylic acids.

The triphenylphosphine complex of palladium in an active catalyst of the carboxylation of ethylene with formation of propionic acid. In the presence of $(PPh_3)_2PhCl_2$ and H_2O at an overall C_2H_4 and CO_2 pressure of 350 atm ethylene is carboxylated at 165 °C with formation of propionic acid, the yield being up to 400 moles per mole of the catalyst introduced[138]. Propene reacts with CO_2 and H_2 only under more severe conditions (300 °C, $p_{CO_2} = 1000$ atm) in the presence of cobalt carbonyl modified with trialkylphosphine and a condensed system incorporating a carboxylic acid and a nitrogen-containing Lewis base; the reaction leads to the formation of 2-ethylhexanal or 2-ethylhexanol[139]. The reaction of CO_2 and H_2 with butadiene in the presence of $Pd[Ph_2P(CH_2)_2PPh_2]_2$ in DMF at 84–120 °C results in the formation of 12.3% of 2-ethylidenehept-5-ene-4-olide:



The reaction is accompanied by the formation of up to 53.3% of polyene-hydrocarbons[140].

Carbon dioxide can also be inserted in the Co–H bond with formation of a formate fragment, which is converted by an alkyl halide into a formate ester. This reaction is also catalysed by the complexes $L_3OS(CO)HCl$, L_3IrHCl, and L_2PtHCl (where $L = PPh_3$).[31] Using as an alkylating agent a solution of BF_3 in CH_3OH, Hashimoto and Inoue[141] synthesised a formate ester via the mechanism

$$L_nMX + H_2 + L_nMH \xrightarrow{CO_2} L_nMOC(O)H + HCOOMe \xrightarrow{MeOH} L_nM(OH) \xrightarrow[-H_2O]{H_2} L_nMH.$$

The reaction proceeds at atmospheric pressure at a temperature of 20–100 °C. The results obtained are presented in Table 6. Group VIII metal (iron, cobalt, nickel, and platinum) hydride complexes catalyse this reaction, which takes place in tertiary amines with a yield of methyl formate up to 23.4 moles per mole of complex[142]. Sodium formate has been obtained in 73.1% yield by the reaction of sodium carbonate or CO_2 with H_2 at a pressure of 108 atm and a temperature of 280 °C. $PtCl_2.H_2O$ was used as the catalyst[143].

Table 6. The synthesis of methyl formate from CO_2 and H_2.[144]

Complex	t, °C	Yield of HCOOCH*	Complex	t, °C	Yield of HCOOCH*
$(PPh_3)_4RuCl_2$	100	9.0	$(PPh_3)_3IrH_3$	100	38.2
$(PPh_3)_4RuCl_2$	20	1.0	$(PPh_3)_3IrH_3$	20	0.9
$(PPh_3)_4RuH_4$	100	4.2	$(PPh_3)_3IrHCl_2$	100	0.2
$(PPh_3)_4RuH_2$	20	0.6	$(PPh_3)_2Ir(CO)Cl$	100	0.2
$(PPh_3)_3RuHCl$	100	17.0	$(PPh_3)_3Os(CO)HCl$	100	0.6
$(PPh_3)_3RuCl_2$	100	9.0	$(Et_3P)_2PtCl_2$	100	0.1

*The yield is given in moles of HCOOMe per mole of the catalytic complex.

In the presence of Group VIII metal complexes secondary amines react with CO_2 and H_2 at 50–60 atm and 100–125 °C with formation of dialkylformamides and equimolar amounts of water[98,144]:

$$CO_2 + H_2 + R_2NH \xrightarrow{\text{catalyst}} HCONR_2 + H_2O$$

The catalysts $CoH(dpe)_2$, $CuCl(PPh_3)_3$, and $IrCl(CO)(PPh_3)_2$, in the presence of which the yield of DMF from dimethylamine reached 1200 moles per mole of catalyst in benzene, showed the highest activity. When n-hexane is used as the solvent, the phosphine complex of ruthenium catalyses this reaction under the same conditions (the yield of DMF is 57.4% [144]— Table 7).

Table 7. The synthesis of dimethyl formamide from CO_2 and an amine[144].

Catalyst	Amount of catalyst, mmoles	Me_2NH, mmoles	t, °C	Yield of DMF*
$(PPh_2CH_2CH_2PPh_2)_2CoH$	1.08	138	100	5
$(PPh_2CH_2CH_2PPh_2)_2CoH$	0.05	131	125	1000
$(PPh_3)_3RhCl$	0.3	122	100	43
$(PPh_3)_3RhCl$	0.02	138	125	170
$(PPh_3)_2(CO)RhCl$	0.38	144	100	1
$(PPh_3)_2(CO)IrCl$	0.35	133	100	28
$(PPh_3)_2(CO)IrCl$	0.2	138	125	1200
$(PPh_3)_2(CO_3)Pd$	0.79	159	100	120
$(PPh_3)_2(CO_3)Pd$	0.7	155	125	104
$(PPh_3)_2Pt$	0.56	155	125	19
$(PPh_3)_3RuCl_2$	0.39	132	125	8
$(PPh_3)_3CuCl$	0.63	133	100	8
$(PPh_3)_3CuCl$	0.03	142	125	900
$H_2PtCl_4 \cdot 6H_2O$	0.56	124	125	11

*The yield is given in moles of DMF per mole of catalyst.

Catalysts based on ruthenium, rhodium, palladium, and platinum are active in the synthesis of urea from NH_3 and CO_2 at temperatures betwen 0° and 300 °C, the presence of small amounts of H_2 and O_2 in the initial CO_2 not influencing the yields of the required product[145].

In solution in a mixture of acetonitrile and ether saturated with CO_2, diethylaminopropyne is converted in 1 h at -60 °C (or at room temperature under CO_2 pressure) into the *N*-methyl-*N*-phenyldiamide of allene-1,3-dicarboxylic acid, the hydrogenation of which on a platinum catalyst gave rise to the *N*-methyl-*N*-phenyldiamide of glutaric acid in up to 85% yield[146]. The continuous synthesis of aminoacids from CO_2 and amines at atmospheric pressure and in the presence of ion-exchange resins is extremely interesting and promising from the practical point of view[146]. Primary and secondary C_1–C_{16} amines, C_1–C_{15} di- and tri-amines, aminoalcohols, and alkyl aminocarbonates readily react with CO_2 at 20–80 °C in the presence of ion-exchange resins of the type Amberlite-45, A-400, 410, IR-45, and Dowex-3 as well as $CuCl_2$ or $Cu(OAc)_2$, forming the corresponding α-aminoacids in up to 85% yield.

Since nitro-groups are powerful electron acceptors, nitroalkanes exhibit in many reactions the properties of a weak acid and are capable of splitting off a proton with formation of a carbanion, which undergoes nucleophilic addition to CO_2 in the presence of alkylcopper complexes[101]:

$$MeNO_2 + RCu(PPh_3)_3 \xrightarrow{-RH} O_2N{-}CH_2{-}Cu(PPh_3)_3 \xrightarrow{CO_2} \rightarrow O_2NCH_2COOCu(PPh_3)_3 \xrightarrow{H_2O} O_2NCH_2COOH .$$

The reaction proceeds via a stage involving the formation of a nitroalkylcopper complex with insertion of CO_2 in the M–C bond and the formation of a carboxylic nitroacid on subsequent hydrolysis with water. This reaction is used nowadays as a model for the investigation of the chemical properties of biotin (vitamin H).[76]

Extremely interesting results have been obtained using sodium phenoxide as a catalyst in the carboxylation of methyl esters of alkanecarboxylic acids with carbon dioxide. The reaction proceeds via a carbanion formation stage. In the presence of sodium phenoxide in DMF at atmospheric pressure and a temperature of 50–70 °C methyl acetate is readily carboxylated with formation of malonate esters (yield 70 to 90%):[147–151]

$$MeCOOMe + CO_2 \xrightarrow[DMF]{PhONa,CH_2N_2} MeCOOCH_2COOMe .$$

Instead of PhONa, it is possible to use the sodium derivatives of *p*-cresol, 3,5-xylenol, and resorcinol[150].

Below 25 °C, sodium phenoxide catalyses the carboxylation of dialkyl ketone to oxoglutaric acid and its derivatives (yield 47–75%):[152–154]

$$MeCMe + 2CO_2 \xrightarrow[DMF]{PhONa} HOOCCH_2C(O)CH_2COOH .$$
$$\quad\quad\quad

IV. INDUSTRIAL PROCESSES WITH PARTICIPATION OF CO_2

In the form of liquid carbonic acid and dry ice, carbon dioxide is used as a cooling agent and a solvent, in the casting industry, and in the synthesis of urea, sodium carbonate, and ammonium carbonate.

Large-scale industrial syntheses based on CO_2 have not so far been achieved with the exception of the industrial method for the synthesis of salicylic and hydroxybenzoic acids by the Kolbe–Schmidt reaction[168]. The *p*-hydroxybenzoid acid and its derivatives obtained by this procedure are widely used in the food, light, and polymer industries.

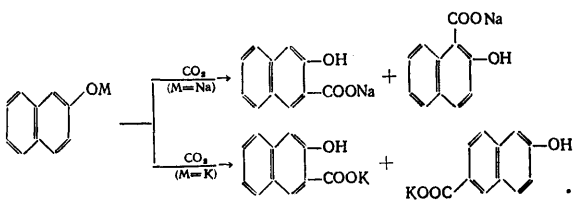
Table 8 presents the results of the carboxylation of sodium phenoxide in a homogeneous system in an aprotic solvent. The reaction proceeds with preferential carboxylation in the *para*-position, while carboxylation in a heterogeneous system takes place with the preferential formation of salicylic acid, i.e. with carboxylation in the *meta*-position. The introduction of potassium into the reaction zone and an increase of temperature to 220 °C tend to increase the yield of the required product above 80%.[169–171]

Table 8. Carboxylation of alkali metal phenoxides (PhOM) in aprotic solvents. ($\tau = 30$ min).[171]

M	Solvent	P_{CO_2}, atm	t, °C	Yield*, %	Compn. of reaction product, %		
					p-hydroxybenzoic acid	salicylic acid	4-hydroxyisopthahlic acid
K	DMF	bubbling	100	24.2	88	12	0
K	DMF	bubbling	150	30.8	83	16	1
K	DMSO	bubbling	100	22.0	94	2	4
K	DMF	5	140	33.5	88	9	3
K	DMF	5	180	41.5	83	13	4
K	DMSO	5	100	23.9	94	2	4
Na	DMF	bubbling	100	10.0	66	32	2
Na	DMF	bubbling	140	22.0	63	36	1
Na	DMSO	bubbling	100	16.5	83	11	6
Na	DMF	5	140	36.1	70	27	3
Na	DMF	5	180	45.4	53	35	12
Na	DMSO	5	140	41.1	81	13	6

*The overall yield of hydroxybenzoic acid and its derivatives is given.

The nature of the alkali metal cation influences markedly the composition of the reaction product. Thus, whereas sodium phenoxide gives rise to salicylic acid, carboxylation of potassium phenoxide under the same conditions leads to a mixture of salicylic and *p*-hydroxybenzoic acids. The influence of the cation on the mode of the reaction involving a series of naphthalene and quinoline derivatives is striking[168]:



The reaction is carried out either by treating the corresponding dry alkali metal phenoxides with CO_2 at 120–130 °C or by heating a mixture of the phenol with an excess of K_2CO_3.

The Kolbe–Schmidt reaction constitutes the main industrial method for the synthesis of salicylic acid from phenol, of aminosalicylic acid from *m*-aminophenol, and of β-hydroxynaphthoic acid from β-naphthol.

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Thus syntheses based on CO_2 make it possible to obtain a wide range of organic compounds of practical importance. At the same time, very few reactions based on CO_2 have been utilised in industry, which is due primarily to the lack of effective carboxylation catalysts[171]. Advances in the field of metal complex catalysis in recent years as well as in the field of the activation of small molecules suggest that active and selective catalytic systems will be developed, on the basis of which the problem of the wide-scale employment of CO_2 will be resolved.

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Changes in Rheological Properties during Formation and Transformation of of Polymers

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Published information on the changes in rheological properties of polymer melts and solutions accompanying various chemical processes—polymerisation, vulcanisation, hardening, gelation—is examined, and experimental methods for the rheological investigation of chemically unstable polymer systems are discussed in detail. Changes in rheological properties should be considered in relation to the chemical kinetics of the processes involved. Technical aspects of the problem are indicated. A list of 133 references is included.

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I. INTRODUCTION

Polymers and compositions based on them provide a most interesting subject for the application of diverse physicochemical methods of investigation, largely because in this class of materials property indices can easily be changed by many powers of ten. Hence the measurement of particular characteristics is a sensitive method of physicochemical analysis of the material. A clear example is given by the rheological properties of polymers, which are highly sensitive to the length of the polymer chain, its structure, the molecular-mass distribution, and the content of the polymer in the system (solution or filled composition).

The general laws of the development of rheological properties by polymer systems as functions of the main determining factors have now been studied in some detail and have been summarised in several monographs[1-3]. Important achievements of the past decade have been measurements on specially synthesised series of monodisperse polymers and their model mixtures[4-10], and also the correlation of numerous and multifarious experimental results on the rheological properties of solutions of various polymers in different solvents throughout the possible composition range[11-18].

The many studies of the past decade have provided a reliable basis for a general quantitative description of the rheology of polymers. They had the common aim of investigating materials that were as pure as possible. Although such an approach is methodologically difficult, it is justified by the comparative ease and unambiguity with which experimental results can be interpreted. Yet this approach ignores several important classes of polymeric materials, among which polymers or polymer systems whose properties vary continuously with time should be specially distinguished. Two significant aspects are firstly that the time taken by these changes is comparable with the duration of observation and secondly that they are functionally inherent in certain polymeric materials, being responsible for their technical value. A fairly large number of cases correspond to these conditions, for time-variable systems are met in various branches of the chemical technology of polymers.

In principle two mechanisms—chemical reactions and physical phenomena—may cause the rheological properties of a material to vary with time. Below we shall consider only the occurrence on an experimental time scale of chemical reactions leading either to the formation of linear polymers or to the conversion of linear polymers (or oligomers) into three-dimensional networks. The process related to the latter case is gelation (gel formation), in which physical changes (primarily crystallisation) may be combined with chemical reactions.

II. METHODS OF INVESTIGATION AND THEIR RANGE OF APPLICATION

Study of the rheological properties of chemically unstable systems during the formation and transformation of polymers is a fairly new field of investigation, which has developed from the traditional rheology of polymers. It is therefore natural that this development has involved the widespread use of customary rheological methods with their appropriate experimental techniques and treatment of the results. However, the need for continuous monitoring of the state of the system has caused a gradual modification of the existing experimental apparatus.

The methodology of the rheology of polymers is based on steady-state and non-stationary measurements. The principles and experimental procedures related to non-stationary methods have been described in detail[19]. Among them only dynamic methods have been widely used for the study of rheologically unstable systems. They consist essentially in subjecting the test specimen to harmonic deformation of specified frequency ω and studying the response of the material in terms of the shear modulus of elasticity G and the mechanical loss angle $\tan\delta$, which depend on ω and, in the case of unstable systems, on the time t.

Relaxation methods have also found an extremely unusual application: it was proposed[20] to use them to monitor the

course of chemical reactions in rubbers subjected to an applied stress. However, this type of approach did not become widespread. Other non-stationary methods for studying viscoelastic properties of polymers were not applied to chemically unstable systems, apparently because of the fundamental difficulty of separating time effects due to relaxation phenomena from those due to chemical changes.

Non-stationary (dynamic) methods for studying chemical changes are used in the following cases—(i) to monitor the initial stage of polymerisation, primarily by means of vibration viscosimeters and procedures identical with those usual in viscosimetry[21]; (ii) to investigate the initial stages of the vulcanisation of rubber mixtures, usually by forced low-frequency vibrations, whose development led to commercial instruments and standardised methods; (iii) to study the hardening of thermosetting plastics and oligomers, especially in practical scientific research using the whole set of modern dynamic methods of measurement; and (iv) to assess the thermal stability of various polymers and to investigate high-temperature processes yielding infusible and insoluble resins.

A fair number of designs and measuring schemes are known that use various instruments operating under dynamic loading at the most diverse frequencies—from infrasonic to ultrasonic—for the above cases. Although various known designs can in principle be used for this purpose[19], the practical importance of thermostable polymers and the difficulties of preparing specimens for investigation led to the establishment of a special method—torsional braid analysis (the TBA method).[22-25]

In the TBA method a bundle of fibres (filaments) is impregnated with a solution of the test polymer. The solvent is then removed, and the usual measurements of modulus or elasticity and mechanical losses are made both on the filament with the deposited polymer and for comparison on a blank filament either under isothermal conditions or with temperature scanning. The properties of the polymer are found by difference, while the observed changes in measured indices enable the variation in state of the test material to be reliably monitored. The convenience of depositing the polymer, the small amount of polymer required, the ease of replacing the fibre braid, and the reliability with which specified temperature conditions are maintained, combined with the proposed[24] automated methods for processing the experimental data, constitute important advantages of this method in comparison with traditional dynamic methods of investigating polymers and give it promise in laboratory practice, especially for investigating newly synthesised polymers.

Steady-state methods of measurement are essentially viscosimetry[21,26] complicated by the fact that polymer systems are not viscous liquids but viscoelastic media[1]. Viscosimetric methods may be used when the test material is able to flow, and their application to the study of chemical processes is possible when the transition period preceding the establishment of steady-state flow and due both to viscoelastic and to thixotropic phenomena[27-31] is significantly shorter than the characteristic time of chemical reaction. In such case many traditional viscosimetric methods prove useful. However, the following substantial difficulties then arise: the deformation produced in any type of viscosimeter can itself have a definite effect on the course of a chemical reaction, and its intensity will depend on the rate of deformation; if the reaction is accompanied by considerable evolution of heat, special attention must be paid to maintaining controllable (e.g. isothermal) conditions of measurement; and in many cases chemical changes in polymers are accompanied by hundredfold and thousandfold changes in viscosity, so that the instrument should be able to measure viscosities of the test medium over a very wide range.

Viscosimetric methods are used industrially for two purposes—(i) to estimate the duration of retention of the fluid state by rubber mixtures (various types of Mooney viscosimeters are used[32]; certain methods of applying them have been standardised in several countries, in particular in the USA as ASTM D-1246, etc. and in the USSR we also have GOST 10 722 as a "method of determining the viscosity and the capacity for premature vulcanisation" of rubber mixtures), and (ii) to measure the "viability" of thermosetting plastics (the rotation viscosimeter developed in the USSR is used for this purpose[33,34]; an instrument of the same type is manufactured also in the Federal Republic of Germany by Gevaert; other suitable experimental methods have been reviewed[35]).

Viscosimetric methods have found very restricted use in the industrial production of polymers (isolated examples can be found[36,37]), despite the exceptionally high sensitivity of rheological indices to the composition of the polymer system and the structure of the macromolecular chain. Polymerisation processes are usually monitored by traditional viscosimetric methods and instruments. However, the problem of studying rapid polymerisation reactions, in particular of assessing the induction period and the intial stages in general, may require the development of scanning methods for monitoring viscosity[38].

The use of instruments combining viscosimetric and dynamic methods of measurement is extremely promising for the investigation of processes starting with a low-viscosity liquid and ending in separation of a solid product, for the whole process of hardening can be examined on a single small specimen. Instruments of this type are now manufactured in Great Britain (the Weissenberg rheogoniometer produced in several modifications by Sangamo Weston Ltd.), the USA (the dynamic spectrometer made by Rheometrix), and in the USSR.[39] An analogous instrument has been developed also for rubber mixtures[40].

III. POLYMERISATION AND POLYCONDENSATION

The change in viscosity and in the whole set of viscoelastic properties of a polymer system during chain growth is extremely striking, as a consequence of the very strong dependence of their governing parameters on the molecular mass and the concentration of the polymer in the solution[1-3], as well as the existence of critical points at which even the character of these relations changes[1,18,41,42]. Indeed, published qualitative results have shown that in actual cases the viscosity of the reaction mass changes by many powers of ten during polymerisation.

Measurements of the viscosity of polymers in the actual monomer are very significant in this connection. The proposed experimental technique makes it possible to follow the course of polymerisation by a dilatometric method with simultaneous measurement of viscosity[43,44]. Results for methyl methacrylate show[45] that the viscosity η is related to the extent of conversion β by the power formula

$$\eta = K\beta^n, \qquad (1)$$

where the constants K and n are determined by the composition of the reaction mass (the concentration of the initiator and the content of the molecular-weight regulator), but all cases show very high values of $n \cong 10$. The polymerisation of butyl methacrylate exhibits a similar $\eta-\beta$ relation, although the region of transition to concentrated solutions of macromolecular products at some critical value of β may be more sharply defined than with methyl methacrylate[46].

An extraordinarily rapid increase in viscosity has been observed also in the copolymerisation of butyl methacrylate with methacrylic acid, although for this sytem the effect is very strongly dependent on the composition of the copolymerising system, and an induction period of almost unchanged viscosity it observed intially[47]. However, evidence of an induction period depends to some extent on the way in which experimental results are presented, which is clearly shown by a comparison of the same data plotted on linear[48] and logarithmic[45] scales. Yet in all the above cases of radical polymerisation the $\eta-\beta$ relation, like the usual dependence of the viscosity of polymer solutions on molecular mass and concentration, undoubtedly consists of two parts—an initial segment with a relatively weak dependence of η on β, and the main segment, when at a considerable degree of conversion the dependence is extremely sharp, and the exponent n reaches very high values.

Extremely interesting experimental results illustrating the way in which viscosity changes during the polymerisation of acrylic monomers in the presence of fillers[49-53] also show change in the rate of increase of viscosity when a certain degree of conversion is reached. It was shown at the same time that the increase is accompanied by a sharp change in the whole complex of rheological properties of the polymerising system, with strengthening viscoelasticity of the solution, evidence of intense structure formation at a certain degree of conversion.

An initially slow and then extraordinarily rapid increase in viscosity of the reaction mass has been observed in the polymerisation of styrene in the actual monomer, which also has a radical mechanism[54] (it is especially interesting to compare these results with an investigation of the rheological properties of the model system formed by solutions of polystyrene of varying molecular mass in styrene[55], which will provide a physical basis for assessing the nature of the rheological transitions accompanying polymerisation). These experimental results[54] were represented by an exponential dependence of viscosity on extent of conversion, but the rheological results for solutions of polystyrene by power functions[55].

It is important to emphasise for the purposes of the present discussion that use of a single variable—extent of conversion—to describe the type of variation in viscosity has proved entirely valid for radical polymerisation under homogeneous conditions.

Unfortunately the above very interesting and significant results were not compared with the kinetics or the mechanism of polymerisation, which would have enabled sound judgments to be made on the relative roles of the main determining parameters—concentration of catalytic system, temperature, and change in the molecular mass of the product and its content in the reaction mass at various stages of polymerisation.

The monotonic character of the variation in viscosity during polymerisation is characteristic only of homogeneous processes. Various physicochemical effects, such as phase separation or inversion at a certain degree of conversion, formation of a heterogeneous system, substantially complicate the pattern of change in rheological properties. A very pertinent example is the formation of shock-resistant polystyrene. An important stage in this process is phase reversal, when at a certain degree of conversion of styrene in the polymer a transition takes place from a system in which the continuous phase is a solution of rubber in styrene to a system in which rubber is dispersed in another, newly formed continuous phase—a solution of polystyrene in styrene—the conditions at this point influencing significantly if not decisively the physicomechanical properties, i.e. the quality of the product.

A fundamental aspect of these problems is that phase reversal is accompanied by a jump in viscosity: the effective viscosity falls very rapidly at the instant of phase reversal (Fig.1 [56]). The drop in viscosity is very clearly evident, since until the critical moment the viscosity has been increasing owing to the polymerisation of styrene (but the polymer remains the dispersed component). The change in character of the variation in viscosity (from increase to decrease) is so marked that it may become an extremely reliable method for the technical monitoring of polymerisation. It should be noted that the viscoelastic properties of the composition change just as sharply at the point of phase reversal, which is evident e.g. in a decrease in the Weissenberg effect.

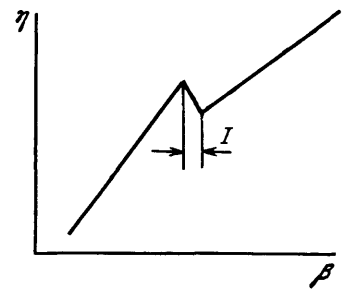


Figure 1. Variation in viscosity during polymerisation accompanied by phase reversal (in the range *I*).

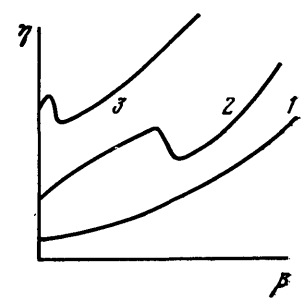


Figure 2. Variation in viscosity during: *1*) homogeneous polymerisation; *2*) phase transition during polymerisation; *3*) heterogeneous polymerisation.

The above example of an extremal change in viscosity at an instant of phase transition during polymerisation is apparently general in character. In this respect special interest attaches to viscosity measurements on methyl methacrylate polymerising in a solvent—precipitant mixture[57]. The composition of the medium was chosen to ensure that polymerisation took place under either homogeneous or transition conditions. Sharp differences were observed in the variation of viscosity (Fig.2 [57])—comparatively slow increase during homogeneous polymerisation (curve *1*), an extremal curve with change in phase state of the system (curve *2*), and a very sharp increase during heterogeneous polymerisation (curve *3*)—the continuance[57] of the relatively slow increase up to extremely high degrees of conversion being due to occurrence of the reaction in solution—not in the mass—so that the polymerising system was a not very concentrated solution.

Isolated qualitative observations show that the moment of phase reversal on formation of an insoluble polymer depends on the rate of mixing of the reaction mass. This is due to both physical causes (since the instant of phase separation depends on the rate of deformation[58,59]) and apparently to the influence of deformation on the rate of polymerisation. The latter is one of the most obscure and little studied aspects of the rheology of polymerising systems. Individual views on this aspect are extremely unconvincing, and there are hardly any "pure" researches in which this question would be studied.

The few investigations in which dependence of rate of polymerisation on deformation of the reaction mass has actually been observed include the discovery of the influence of rate of shear on rate of change of viscosity during the cross-linking of oligourethane[60]. However, the complexity of interpreting the results, consequent on the extremely specific character of the dependence of the effective viscosity of an oligomer on rate of shear, prevents their extension to other polymerising systems in general. Thus a region of dilatant behaviour—increase in effective viscosity with rate of shear—is often observed[60,61] with oligomers at low rates of shear. Significantly different flow curves are observed for concentrated solutions[1,6,13,18]. Therefore the type of dependence of viscosity on rate of shear changes as polymerisation proceeds, so that viscosity measurements with a constant rate of shear (as in Ref.60) may give points corresponding to different regions of the flow curve of the reaction mass, which makes their comparison ambiguous.

The character of the variation in viscosity depends on the mechanism of polymerisation, since the variation of the two principal factors—the mean molecular mass of the product and the polymer content of the reaction mass—is determined by this mechanism. The physical state of the specimen—whether it remains a solution during polymerisation or whether the system becomes heterogeneous, which very strongly influences the rheological properties—also depends on the nature of the reaction medium. Unfortunately, very little attention has been paid to these question: the few experimental results are qualitative in character and are in no way linked with the mechanism or the kinetics of polymerisation, although simple semi-quantitative considerations clearly indicate that the kinetics of polymerisation play a decisive part in the variation of the viscosity[62].

If polymerisation has a radical mechanism, the initial mean degree of polymerisation remains constant during a fairly lengthy initial stage[63], while the yield of polymer increases linearly with time. In terms of the governing parameters this implies that the initial stage consists in a temporally linear increase in concentration of polymer in solution. Hence the expected character of the variation in viscosity can be indicated, provided that the concentration dependence of the viscosity of solutions of specific composition is known. Experimental results make possible such an analysis, which has recently been made and has confirmed the validity of the suggested theoretical approach[64]. A more complete scheme of radical polymerisation must take into account the time variation of the mean molecular mass, which depends on the relation between reactions of chain growth and transfer. In any case, however, a detailed kinetic scheme of a specific radical polymerisation together with the constants of the elementary reactions provides sufficient basis for assessing the way in which the viscosity changes during polymerisation. Nevertheless, such an approach is valid as far as the gel point, which also can be detected by rheological methods and is associated with certain peculiarities in the viscosity properties of the reaction mass[65] or with change in the free volume as a factor determining the rheological properties of the polymerising system[66].

Another kinetic scheme, involving an ionic mechanism of polymerisation[67-69], is most simply represented by chain growth at a certain number of active centres, whose concentration A remains unchanged during the reaction, while chain termination is excluded. If the degree of conversion determined from the change in concentration of functional groups is β, the mean molecular mass of the resulting polymer is at some time proportional to the ratio β/A, while the concentration of polymer in solution is proportional to β. Thus both the molecular mass and the polymer content of the solution change, in contrast to the preceding case. This situation becomes substantially more complicated if the polymer separates from solution, which, of course, affects the rate of increase of viscosity[69].

Finally, in a specific kinetic scheme based on chain growth by a polycondensation mechanism all molecules are simultaneously involved in the increase in molecular mass, and the degree of conversion β corresponds to the mean degree of polymerisation $(1-\beta)^{-1}$, but the polymer concentration in solution during polycondensation is constant at unity. This implies that the course of changes in the governing parameters is significantly different during polycondensation than during radical or ionic polymerisation.

Dependence	Radical mechanism	Ionic mechanism	Polycondensation
$\bar{P}(\beta)$	1	β	$(1-\beta)^{-1}$
$c(\beta)$	β	β	1
$\eta(\beta)$	β^b	β^{a+b}	$(1-\beta)^a$

Thus the effects on variation in viscosity η of different types of dependence of mean degree of polymerisation $\bar{P}$ and concentration c on degree of conversion β is determined by the type of function $\eta(c,\bar{P})$. If it is assumed for illustration[1,18] that $\eta \propto \bar{P}^a c^b$ (where a and b are constants), the above effects of the mechanism of polymerisation on variation in viscosity can be summarised as in the Table. Although the degree of conversion β is the sole governing parameter in all cases, the character of the function $\eta(\beta)$ varies substantially depending on the mechanisms of formation of the polymer.

The above simple schemes of growth in viscosity during polymerisation apply to isothermal conditions. Non-isothermal phenomena during polymerisation exert a significant influence on changes in rheological properties, and may lead to completely novel non-trivial effects (a detailed survey of related problems has appeared[70,71]). Some of these cases, e.g. the changes in viscosity during adiabatic polymerisation, can be described quantitatively[62]. To obtain a more general description requires a very large body of calculations, which can be justified by the fundamental interest of the problem and for applied purposes. However, it is important that in all cases such calculations should be based on detailed knowledge of the kinetics of polymerisation, and also on establishment of the way in which viscosity depends on the molecular mass of the polymer and the content in the solution, for specific cases of theoretical or technical interest.

IV. VULCANISATION OF ELASTOMERS AND HARDENING OF THERMOSETTING PLASTICS

Elastomers and thermosetting plastics are both able to react to form a three-dimensional network of chemical bonds, with conversion from a liquid to a non-fluid and infusible material. It is this transition, in which all the rheological properties change within wide limits, that we shall discuss here. The most characteristic changes consist in an increase in viscosity to "infinitely" high values, an extremal change in hyperelastic properties at a stage preceding formation of a continuous three-dimensional network of chemical bonds[72,73], and ultimately the appearance of an equilibrium modulus characteristic of non-fluid systems. The components of the dynamic modulus of elasticity also change. Such changes are strongest at low frequencies, since the development of properties then involves movement of the macromolecular chain as a whole or of quite long segments. Formation of cross-links, however, hinders movement of the chain more strongly the larger the portion of it is involved in the elementary act of relaxation.

The great changes in rheological properties of oligomers during hardening or of rubbers during vulcanisation have formed the basis of various industrial methods for monitoring structural transformations by measuring the rheological (or mechanical) characteristics of the material. Among them the best known and quite widely used are methods for monitoring the vulcanisation of rubber mixtures using various designs of Vulcameter, Curometer, etc., as well as dozens of industrially produced and standardised, and also home-made, devices employing the most diverse types of loading. The initial stages of vulcanisation are usually monitored viscosimetrically, but the continuation of vulcanisation (hardening) after formation of the three-dimensional network of chemical bonds is recorded by dynamic methods. The chief experimental methods and modes of treatment of the results applied to rubbers and rubber mixtures for this purpose were summarised in a monograph[32].

The further efforts of investigators in this field are now directed at standardising test conditions and procedures as strictly as possible, achieving reproducible comparative results, and establishing correlations between characteristic points in relations obtained in different types of apparatus and technical indices of the moulded articles. In the immediate future we must even expect strengthening of the requirements for the standardisation of conditions of measurement together with automation of instruments used in industrial practice.

Study of the rheological changes accompanying the hardening of oligomers is in a somewhat different position. The specific nature of problems arising here is most conveniently illustrated by the example of epoxy-resins, whose hardening has been studied by means of the whole set of existing rheological methods. Hardeners of amine type have been used in most of this work.

Investigation of the initial stages of this process requires primarily the determination of viscosity—temperature—time ($\eta-T-t$) characteristics for multicomponent materials having various compositions[74-81]. A constant-temperature cross-section of such a characteristic can be represented schematically by the graph in Fig.3. The greatest interest attaches to assessment of the positions of two points: the time t_0 defines the "viability" of the oligomer, i.e. the duration of the low-viscosity liquid state; and the time t^* corresponds to the attainment of a certain high viscosity, which in practice is defined as "gelation", i.e. the point at which fluidity is lost, although the polymer actually remains fluid for some time longer. The gelation point is determined by the accepted arbitrary technical methods and corresponds[74] to a very narrow viscosity range (~1200–1400 P). This result gives a quantitative basis for the technical estimates of t^* adopted in practice, which is important when considering non-isothermal hardening schedules for thermosetting resins. Nevertheless, this viscosity criterion is fairly arbitrary, for the mouldability of compositions based on epoxy resins is determined[75] by a viscosity of only 500 P, as was demonstrated for many systems differing in composition.

It is important to observe that in general there is no correlation between t_0 and t^*. Consequently the "viability" of a material is still an inadequate indication of its technical possibilities, and the ability to be moulded may be retained for a long time (between t_0 and t^*) if the increase in viscosity during this period is not very rapid. Therefore the complete time dependence of viscosity $\eta(t)$ must be used to assess the technical properties of compositions.

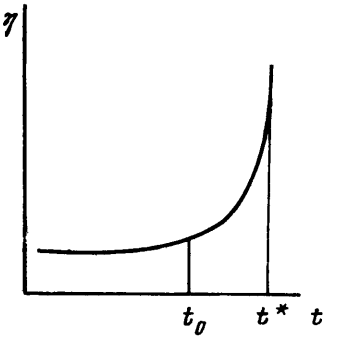


Figure 3. Assessment of critical points—"viability" and "gelation" times—in the hardening of oligomers.

The graph in Fig.3 can be expressed analytically in various ways depending on the specific hardening reactions of actual oligomers. Often this relation is clearly described by means of an exponential function:

$$\eta=\eta_0\exp(kt), \qquad (2)$$

where η_0 is the initial viscosity and k the kinetic parameter of hardening, both of which depend on the temperature. An exponential time variation of viscosity usually "works" quite well in the initial range, but not as far as the gelation point, for the increase in viscosity accelerates as this point is approached. More complicated $\eta-t$ relations have also been suggested[78,79] which take into account the very sharp increase in viscosity in the hardening of epoxy resins.

The hardening of oligomers often takes place under non-isothermal conditions. It is therefore important to generalise formula (2), so that complete $\eta-T-t$ hardening characteristics can be obtained. For this purpose the temperature dependence of η_0 is expressed in the usual way:

$$\eta_0=\eta_\infty\exp(E_\eta/RT), \qquad (3)$$

where E_η is the activation energy of viscous flow and η_∞ a constant. The temperature dependence of the rate constant

k is described similarly, but with a different activation energy E_k, of hardening:

$$k=k_\infty \exp(E_k/RT). \quad (4)$$

Then

$$\ln\eta=\ln\eta_\infty+E_\eta/RT+tk_\infty\exp(E_k/RT). \quad (5)$$

Direct measurements have shown[74] that $E_k \approx 200$ kcal mole^{-1} for the hardening of epoxy resins with amine hardeners, while E_η varies with the composition of the materials from 22 to 41 kcal mole^{-1}. Both η_∞ and k_∞ are also strongly dependent on composition.

Formula (5) can be used to estimate the gelation time t^* under non-isothermal conditions. This is important technically, since actual hardening processes almost always take place under non-isothermal conditions and go to completion fairly rapidly, so that their direct observation is difficult. The appropriate generalisation is made by replacing kt in Eqn.(2) by the expression

$$\int_0^t k(T)\,dt = k_\infty \int_0^\infty \exp[E_k/RT(t)]\,dt. \quad (6)$$

Then

$$\ln\eta = \ln\eta_\infty + E_\eta/RT + k_\infty \int_0^t \exp[E_k/RT(t)]\,dt. \quad (7)$$

The integral on the right-hand side of (7) is evaluated (for a specified programme of temperature variation) by any numerical method†.

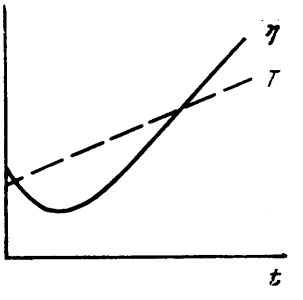


Figure 4. Variation in viscosity during non-isothermal hardening (linear time variation of temperature).

In practice a linear (or almost linear) time variation of temperature of a composition is often achieved. This gives a characteristic extremal variation in viscosity (Fig.4), due to competition, with rise in temperature, between softening (lowering of viscosity) and acceleration of the chemical reaction. Use of the generalised $\eta-T-t$ characteristic in formula (7) enables a correct estimate of the gelation time t^* to be made in this case, and an optimum hardening schedule to be selected by varying the rate of heating.

One factor restricting the possibility of increasing the rate of rise in temperature and thereby accelerating the technical process is the requirement that the temperature gradient across the mass must be lowered in the moulding of large or thick-walled articles. With external heating a uniform temperature field throughout the article cannot be guaranteed, so that hardening takes place non-uniformly, which leads to the appearance of considerable (or even unacceptably high) internal stresses. Therefore the choice of optimum rate of rise in temperature during the hardening of oligomers must take into account the heat-transfer conditions in an article of specific dimensions and the estimated internal stresses arising during heating, chemical reaction, and cooling.

The construction of $\eta-T-t$ characteristics has general value for analysing the non-isothermal hardening of thermosetting resins, compositions based on them, and other rheologically unstable materials undergoing particular chemical changes when heated. The fairly large number of studies of the changes occurring in the rheological properties of oligomers during hardening suggest a single type of behaviour governed by two characteristic indices—the duration of the initial ("induction") perod of slight increase in viscosity and the gelation time.

The possibility of the temperature—time superposition of chemorheological characteristics of polymer materials also has general value. It implies that the generalised time characteristic of the variation in viscosity can be constructed as a function of the product ta_T, where a_T is the temperature dependence of the rate of hardening. Direct measurements have shown[80] that a_T is described in terms of the same activation energy as that characterising the temperature dependence of the viscosity of the oligomer in the initial state. Apparently, however, this is not a universal rule, as has been emphasised above (the dependence of the activation energy of viscous flow on the composition of the hardened material with E_k unchanged during the hardening of epoxy resins by an amine type of hardener). Nevertheless, the possibility of applying temperature—time superposition in those specific cases in which it applies in practice provides an important method for constructing $\eta-T-t$ characteristics and enables technical parameters of a composition to be estimated at temperatures at which direct measurements cannot be made because of the high rates of hardening.

The relation between the activation energies of viscous flow and chemical reaction E_η and E_k is important in the consideration of changes in viscosity during non-isothermal hardening. In general these constants can be regarded as independent, and the general $\eta-T-t$ characteristic described by formula (7) can be used. The postulate that the change in viscosity due to hardening and the role of temperature as a factor controlling the rate of chemical reaction are far stronger than the actual temperature dependence of viscosity at a certain stage of structure formation is apparently legitimate and extremely useful in virtue of the equations it gives[81].

In essence this hypothesis is sufficient for the temperature—time superposition of $\eta-t$ relations obtained at different hardening temperatures. Hence follows in particular the possibility of estimating the activation energy (or the temperature dependence of the rate of chemical reaction in general) from the temperature dependence of the duration of reaction necessary to achieve a specified viscosity. Application of this approach to various thermosetting resins gave positive results. Thus the activation energy of the process characterised by the time variation of the viscosity of a resol agreed with the value found by an independent chemical method[82]. It was shown for epoxy resins that the activation energy of the process leading to the increase in viscosity was independent of the actual viscosity at which the corresponding duration of reaction was compared. The activation energy thus obtained from viscosimetric data was almost identical with the value found from a chemical study of the kinetics of hardening[81].

† The possibility of such an approach has recently been extended also to non-isothermal increase in viscosity of a polyester binder[113].

However, such a simple approach is restricted to the state of viscous flow: on the formation of non-fluid materials the possibility of temperature—time superposition becomes debatable. This is indicated by the differences observed between activation energies calculated from the induction period and from the gelation time[81]. Nevertheless, such differences may be fortuitous, in view of the ambiguity in the assessment of the instant at which fluidity is lost, since this point is actually determined from arbitrary indices.

The complexity involved in characterising the rheological properties of hardening polymer materials is due not only to the need to estimate changes in behaviour of the specimen with time but also to the fact that the test materials (except perhaps during the initial state) exhibit an anomalous viscosity effect, with the departure from Newtonian flow changing with the degree of structure formation. Therefore the problem of describing the flow of hardening polymers is of intrinsic value. The early papers[83,84] used the Bingham model of a viscoplastic medium to represent the viscosity properties of compositions based on phenol—formaldehyde resins. Actually, however, a true fluidity limit is most likely absent from such compositions until a three-dimensional network is formed[85,86], although a definite part may be played by the nature of the filler used, interaction of whose particles may lead to the appearance of solid properties in the compositions[87,88]. In such cases the appearance of a fluidity limit is not directly due to hardening of the oligomer, in contrast to what occurs during structure formation causing the gelation of polymer solutions[89]. Nevertheless, it is not always possible to draw a sharp boundary between these two phenomena.

A high filler content in hardening oligomers, even if it does not tend to form a stable structural network, leads to the boundary-layer slippage characteristic of highly filled compositions when they are forced through moulding channels[90,91]. In actual technical situations and in the laboratory investigations simulating them the dominant role in the hydrodynamic resistance of the channels is played by boundary-layer slippage until high degrees of structure formation are reached. The role of the filler is especially important in the flow of hardening compositions in the region of sharp changes in cross-section of the channel, e.g. in the entry portion of moulding channels[92], where a decisive part is played by the presence of the filler, not by hardening of the oligomer[92,93]. Boundary-layer slippage or rupture of the deformed composition occurs with various flows of highly filled oligomers[94], but this effect is not specific to hardening materials, since completely analogous phenomena are observed in the flow of various polymer materials[4,5,90,91].

The reliability of viscosimetric analysis for kinetic study of the hardening of oligomers largely depends on how far the change in properties of the specimen can be separated from thermal effects due to the exothermic character of hardening. The importance of this factor is clearly indicated by kinetic results for phenol—formaldehyde resins, which enabled their viscosity to be related to the extent of conversion[95,96]. Extrapolation of the results to "zero" specimen thickness proved that the induction period always observed in practice is not a true kinetic effect but is due to delay in the spread of temperature throughout the specimen. It has already been suggested above that the inevitable non-uniformity of the temperature field (and hence degree of conversion throughout the specimen) is a cause of internal stresses. Here another aspect of non-isothermal hardening is emphasised—as a factor complicating kinetic interpretation of the results—so that correct allowance for non-isothermal effects achieved by different methods[97-99] has general value for a whole range of problems associated with the changes in rheological properties of polymer materials undergoing structure formation.

Successive separation of thermal effects from the change in degree of hardening has shown that the increase in viscosity in the initial stages of structure formation in phenol—formaldehyde resins is described by the formula[90,91]

$$\eta=\eta_0(\beta)\exp(E/RT), \tag{8}$$

in which the pre-exponential factor $\eta_0(\beta)$ represents the effect of degree of conversion β on viscosity, while the activation energy $E = 8.22$ kcal mole^{-1} is almost independent of β until a considerable degree of conversion is attained. The maintenance of an unambiguous relation between degree of conversion and viscosity whatever the thermal history of the material is very important, since it enables a single main reaction to be regarded as causing the increase in viscosity. It is also responsible for the possibility of finding generalised $\eta-T-t$ characteristics in the form (7).

A similar approach to describing the degree of conversion attained as the sum of changes occurring with different laws of variation in the temperature of the material is valid also for rubber mixtures[100].

Another important aspect of the rheology of hardening compositions related to the non-isothermal character of flow is the influence of rate of deformation on kinetics of hardening. This problem has been very little studied, and existing data are unreliable just because effects due to the actual increase in rate of deformation and to the consequent evolution of heat (corresponding to the rise in temperature and in the rate of hardening) were not separated. Therefore the shortening of the time during which an oligomeric composition remains plastic, with increase in the flow rate of shear[101-103], may actually be due to non-equivalence of the temperature conditions of deformation. This is indicated also by the marked effect of initial temperature on the development of the effect, which may be associated with the viscosity of the oligomer: the higher the temperature the lower the initial viscosity of the reaction mass, and hence the smaller the evolution of heat at comparable rates of deformation and the weaker the influence of flow on the reaction kinetics. Therefore the influence of deformation on the course of the hardening of oligomers remains an open question.

It is very tempting to simplify the description of processes occurring in the initial stages of the hardening of oligomers by using a single parameter, e.g. the degree of conversion. This is possible if any leading mechanism of chemical changes in the reaction mass can be distinguished. Viscosity measurements during the formation of polyurethane are significant in this respect, when the precise meaning of the reaction mechanisms enabled the viscosity to be related to the molecular characteristics of the product at various stages of polycondensation[104].

Kinetic study of the hardening of oligomers by viscosimetry is mainly of value for the initial stages, which in practice correspond to preparation of the composition or decomposition of a hardening layer on a reinforcing material. Subsequent stages extending as far as the final article can conveniently and fruitfully be observed by a dynamic method, by measuring the time variation of the modulus of elasticity G and the mechanical loss angle $\tan\delta$.[105]

The most general picture of the variation in dynamic characteristics during hardening has been obtained with epoxy resins. It is shown diagrammatically in Fig. 5,[106] where the upper continuous curves represent the variation in the glass

point T_{gl} during vitrification, and t_{gl} is the length of the hardening period necessary to reach the region of vitrification. Analogous results (but not so complete) conforming to this pattern have been obtained by other workers[107,108]. In order to understand the results of rheological investigations on this process it is fundamentally important that we establish the relationship between three temperatures—that of the experiment T, the glass point of the unhardened composition T_{gl}, and the glass point of the final product $T_{gl,\infty}$—bearing in mind that achievement of maximum loss than δ corresponds to the relaxation transition point.

We may suppose, for example, that condtions of vitrification are attained before the gelation point (i.e. at $T < T_{gl}$). Maximum tan δ then corresponds to some degree of structure formation, and an already vitrified polymer will undergo only a slight decrease in tan δ as the process continues. Another case corresponds to the condition $T_{gl} < T < T_{gl,\infty}$, when two loss maxima are observed: the first occurs at the gelation point, i.e. on transtion from a fluid to a hyperelastic state, and the second at the glass point, i.e. the main relaxation transition. Finally, in the third case, with $T > T_{gl,\infty}$, gelation conditions are reached very rapidly (because of the high temperature), but vitrification does not take place: i.e. the material is in a hyperelastic state the whole time. This extremely informative view of the changes in dynamic properties of a composition is generally valid for the hardening of oligomeric resins. Important technical recommendations for two parameters—gelation time t_0 and vitrification time t_{gl}, the latter close to the time at which hardening is complete—can be obtained from this scheme. Taking Fig.5 to represent a model of the process, we can analyse the specific features of the hardening of various materials.

The fertility of applying a dynamic method to analyse the concluding stages in the formation of a rigid polymer has been demonstrated in estimating the degree of cyclisation when a polyester–amide film is heated to give a polyimide[109]. Measurements of the time dependence of the dynamic modulus of elasticity can usefully be employed for studying the induction period, the duration, and the completion of the linear and three-dimensional copolymerisation of organosiloxane monomers[110]. Interest attaches also to a recently developed method for analysing chemical changes in solid polymers by introducing a reactive component into the matrix of a heat-resistant rigid polymer: occurrence of a chemical reaction in the material, including intrachain processes, can be assessed from the variation in dynamic mechanical properties (loss angle and elastic modulus)[111,112].

The above results clearly show the possibility and the value of a dynamic method for investigating chemical processes in structure-forming oligomers and monomers. Therefore this method is readily used to monitor various real technical processes: for example, it has been proposed[113] to employ measurements of dynamic properties in the acoustic frequency range to monitor the completion of hardening in articles made from thermosetting resins and glassfibre-reinforced laminates based on them. A qualitative similarity was found[113] in the changes in acoustic (i.e. ultimately elastic) properties of binder and laminate. Although the type of time dependence of the measured signal varies, the positions of characteristic points corresponding to formation of a three-dimensional structure in the polymer and to completion of hardening almost coincide for polymer and composition based on it. Therefore use of a dynamic (e.g. acoustic) method will permit non-destructive monitoring of the concluding stage in the hardening of the polymeric binder in glass laminates. Such a method has been successfully used also to monitor foaming and subsequent hardening of polyurethane foam plastics[114].

A dynamic (or vibrational) method can also be used to monitor the vulcanisation of rubber mixtures, especially the hardening of liquid rubbers[115], when a complete change in modulus of elasticity can be observed, from low values corresponding to the liquid state right up to values in the region of the hyperelasticity plateau. However, a dynamic method will give entirely reliable results even for ordinary highly viscous rubber mixtures. This has permitted standardisation of a dynamic method for monitoring the vulcanisation of rubber mixtures (ASTM 2704–2706 in the USA), and a good correlation was shown[116] between values obtained by this method and by the customary but more inconvenient and less sensitive and reliable Mooney measurement of coefficients of viscosity.

Dynamic effects on the test material involved in non-destructive monitoring methods do not themselves in any way affect the kinetics. However, this does not limit the possibilities and prospects of applying dynamic (or vibrational) effects on structure-forming compositions, in particular thermosetting plastics. In fact, with increase in amplitude of deformation and transition to so called "large" amplitudes

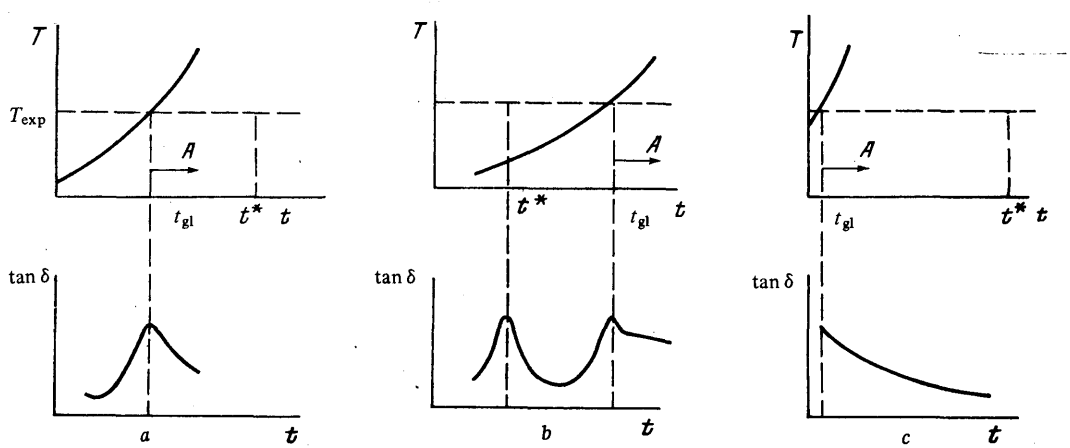


Figure 5. Variation in dynamic properties during hardening for different relations between experimental temperature and glass point: *a*) $T_{exp} < T_{gl}$; *b*) $T_{gl} < T_{exp} < T_{gl,\infty}$; *c*) $T_{exp} > T_{gl,\infty}$; *A*) the arrow indicates the region of the vitreous state of the material.

(in contrast to the "infinitesimal" amplitudes used for non-destructive measurements) vibrational effects become an efficient means of influencing the kinetics of chemical processes. This has been clearly demonstrated on the same epoxy resin[117]: increasing the amplitude of deformation led to a sharp fall in elastic modulus and to a delay in hardening, but the final state of the polymer subjected to vibration was characterised by a higher modulus. Cyclic deformation with large amplitudes presumably delays formation of a three-dimensional network of chemical bonds and intensified hardening.

Unfortunately the paper[117] gives only limited information on this interesting and promising aspect of the reality of structure-forming polymer systems. There is thus no basis at present for discussing how general is the significance of these facts. Undoubtedly, however, the use of large-amplitude dynamic effects can give important new information on the behaviour of polymer compositions during hardening and is of definite technical interest for controlling the rate of hardening and the properties of the end-products.

V. GELATION

Gelation is intermediate between polymerisation in solution and vulcanisation with respect to the accompanying change in rheological properties. The initial stages actually involve an increase in viscosity owing to chemical interactions of a limited number of macromolecules, which results in an increase in molecular mass of individual chain structures. Then a single three-dimensional network appears, which contains a considerable proportion of the initial chains, while the remaining solvent acts as a plasticiser of the rubberlike structure[118,119]. In the light of the above rheological approach, therefore, gelation involves conversion of a relatively low-viscosity liquid into a viscoelastic medium incapable of flow, regardless of the actual mechanism of gelation, which may be associated not only with chemical reactions but also with physical transitions (e.g. formation of microcrystalline regions).

The variation in viscosity during gelation has quite long been regarded as an extremely sensitive indication of the course of the process. Moreover, a rapid increase in viscosity with time has been interpreted as a criterion of conversion of the solution into a gel. Quite frequently, indeed, e.g. for ethanolic solutions the cellulose nitrate[120] or for aqueous polyacrylic acid[121], the variation in viscosity is extremely simple: a prolonged stable state or slight growth in viscosity is replaced by a very rapid fall in fluidity. The length of the induction period depends on the temperature, but the whole observed pattern of change in viscosity resembles so strikingly the kinetics of crystallisation of a polymer from solution that it can be regarded as indirect evidence of gel formation by a mechanism of crystallisation. More complicated cases of growth in viscosity with time are known, when the rate of change decreases[122].

However, known examples of increase in viscosity during gelation are partial in character, while possible ambiguity of results and interpretations based on viscosity measurements is due to ambiguity in the very concept of "viscosity" for non-Newtonian polymer solutions. The actual pattern of variation of viscosity properties during transition of a solution into a gel is substantially more complicated. As has been shown for gelling solutions of a polysulphonamide in dimethylacetamide[89], the way in which viscosity varies with time depends markedly on the conditions under which the measurements are made (Fig. 6): at high rates of shear the viscosity increases only slightly for a long time, and gives hardly any indication of the occurrence of gelation. Yet the possibility of gel formation may already have been established, if the clearest criterion of gelation—a yield point in a homogeneous system—has appeared. And then, if measurements are made at low rates of shear, a clear structure-formation effect is observed.

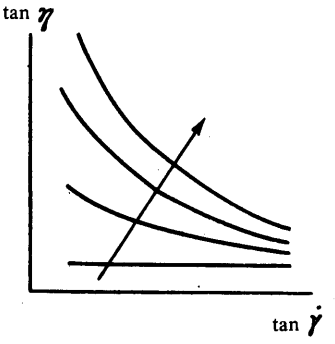


Figure 6. Variation in dependence of viscosity on rate of shear $\dot{\gamma}$ during gelation. The arrow shows the direction of increase in duration of the process.

Here we must emphasise the difference between the "state" and the "behaviour" of a material. In general this difference is well known for polymers: thus a polymer in a hyperelastic state may behave as a glass, but a melt as a rubber[2], which is a direct consequence of the relaxation mechanism of polymer deformation. The same applies to the solution—gel case. The existence of a yield point should in general be regarded as a criterion of a gel[89,119]. However, the appearance of a yield point (or a limiting shear stress) can have various causes. Thus in dispersions with a polymeric binder a solid filler may form a structure that undergoes brittle fracture at some critical stress[123]. A still closer approach to gels is made by liquid-crystalline polymer solutions, in which a well defined though not very high yield point is observed[124-126].

The borderline between jellies and other systems having a yield point is fairly arbitrary. But in any case the states of a system below and above the yield point must be distinguished. In this sense it is more correct to speak, not of the "state" of solution or gel, but of behaviour equivalent to "solution" or "gel" behaviour. However, even the transition between "fluid" and "non-fluid" states may be blurred if breakdown of the structural network formed by macromolecules takes time, i.e. if this network possesses durability[127].

From the rheological point of view transition to the gelatinous state is complete when the yield point, which increases during gelation, becomes equal to the tensile strength of the material, so that the possibility of transition to a fluid state has completely disappeared[89].

Gelation is characterised by the appearance not only of a yield point but also of a set of thixotropic properties, which in the early stages of gel formation are studied by the same rheological methods of rotational rheometry[128] as are thixotropic changes in polymer melts and solutions[129]. At the stage of formation of a three-dimensional structure the thixotropic properties of gels are observed by dynamic methods—from the time variation of the modulus of elasticity[130].

Furthermore, deformation may itself affect the rate of gelation[131], so that the introduction of shear in the measurement of viscosity is an active factor influencing the kinetics. Therefore viscosity measurements, especially if they are approached without sufficiently thorough analysis, are insufficient to assess the changes accompanying gelation. Additional information may, of course, be obtained by measuring the hyperelasticity or the viscoelastic properties of the material, which also change on formation of a jelly. But it is also relevant that in some cases rheological methods may be relatively insensitive to structural changes.

An investigation of gelation in gelatin solutions[132] has given results that are significant in this connection. Spectroscopic observation showed that, in the initial stage of structure formation, changes in intensity of several bands occured for ~6 h, indicating the occurrence of chemical reactions. These changes are entirely susceptible to the usual kinetic interpretation: they are described by a first-order equation with rate constant 0.01 min^{-1}. The viscosity, however, remains almost unchanged during this period, and increases significantly only after 9—10 h, a considerable time after completion of the chemical changes observed spectroscopically. Thus macroscopic changes (apparent in an increase in viscosity) do not necessarily follow all the microscopic processes. In the present case spectroscopic observations enable nucleation within individual molecules to be followed, whereas the viscosimetric method indicates the combined effects of intermolecular interactions—the formation of spiral multimolecular structures.

In concluding this discussion of jellies as systems undergoing changes in rheological properties during formation it must be emphasised that, despite the huge literature (a 1974 review[104] contains 399 references), very few systematic quantitative investigations of rheological changes in a system during gelation have been made, and available information is restricted to a number of particular examples.

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This Review of published experimental facts and theoretical aspects of the changes in rheological properties accompanying polymerisation and the reactions of polymers and compositions based on them shows that the variation in all the rheological indices is regularly linked with the molecular characteristics of the polymer. This opens up wide possibilities for the use of rheological measurements for monitoring and controlling technical processes in the production of polymer materials and chemical stages in the moulding of articles (hardening, vulcanisation, etc.).

Until now this important and promising field has not received due development. The reasons are inadequate study of the relations between rheological characteristics and molecular parameters of specific and diverse materials, little attention paid to several fundamental problems, in particular the influence of rate of deformation on the kinetics of chemical processes, the absence or inadequacy of experimental technique, especially in controlling the technical process, and the absence of a general theoretical approach to the design of reaction vessels in which properties of the medium change significantly (in many cases even radically). Solving these problems will permit effective utilisation of rheological methods in the production and processing of polymer materials.

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Surface Electrical Characteristics of Disperse Systems Containing Polymers

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Studies of the effect of the adsorption of non-ionogenic polymers from aqueous solution on the surface charge density, electrokinetic potential, and surface conductance of dispersed particles are summarised, and theoretical ideas on the mechanism of the effect are examined. Methods for calculating the parameters of adsorbed layers of polymers from surface electrical measurements are described and analysed. A list of 84 references is included.

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I. INTRODUCTION

The interest in disperse systems containing polymers, displayed during recent years by research workers in various countries, is due to the important part played by such systems in various branches of modern industry. Water-soluble polymers are finding ever wider application as effective flocculants and stabilisers, binders and plasticisers, structure-regulating agents. Yet the mechanism of the influence of macromolecular compounds on various properties of disperse systems has been by no means fully studied, while theoretical principles for the selection and application of polymers for the above purposes are at an early stage of development.

It is generally known that the fundamental process largely determining the behaviour of disperse systems containing additions of polymers is adsorption interaction of macromolecules with the particle surface of the dispersed phase. Therefore investigation of the adsorption and the structure of adsorbed layers of polymers will help to reveal the mechanisms of the influence of macromolecular substances on various properties of dispersions, in particular the stability of their state of aggregation.

At least three main parameters—(*a*) the total adsorption, (*b*) the number or proportion of chain units in contact with the adsorbent surface, and (*c*) the density distribution of units normal to the surface or, as a first approximation, the thickness of the adsorbed layer—must be known for a description of the structure of an adsorbed layer of a macromolecular compound[1]. Usually no difficulty arises in determining the first of these parameters, but special methods are required to find the other two.

Macromolecules adsorbed on a heteropolar surface may influence substantially the structure of the electrical double layer; and potentials and charges on the latter in turn affect the conformational state of the macromolecules. Lyklema[2] has postulated that modification of the dense region of the double layer is due to the adsorption only of monomer units in direct contact with the surface, whereas changes in the diffuse region are caused by segments of adsorbed macromolecules extending into the solution as loops and spikes. Fig.1 gives a schematic picture of the adsorption of polymer macromolecules on a heteropolar interface[2]. It undoubtedly represents only a first, extremely crude approximation, but nevertheless enables the position to be understood. Lyklema's division of "spheres of influence" is also arbitrary, since changes in structure of the two regions of the double layer are interrelated.

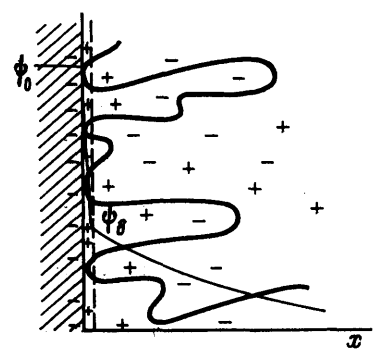


Figure 1. Diagrammatic representation of macromolecule adsorbed on a heteropolar interface, together with the variation in the ψ_0 and ψ_δ potentials with distance x from surface[2,12].

The fact that the adsorption of polymers affects the structure of the electrical double layer makes it theoretically possible to study the structure of adsorbed polymer layers by a combined investigation of the surface electrical characteristics of dispersed particles. Such investigations have been made by electrochemists at a mercury electrode, and a bibliography on this topic can be found in Ref.2,

but for disperse systems this method is novel and promising. Formation of an adsorbed layer of a macromolecular compound leads to a change in several surface electrical characteristics—surface potential and differential capacitance of the double layer, potential of the Stern layer, and the dielectric constant of the surface layer of solution—but the influence of the adsorption of polymers is usually studied on those parameters of the double layer that are susceptible to experimental determination, i.e. the surface charge density σ, the electrokinetic potential (ζ-potential), and recently the conductivity of dispersions. The present Review summarises results largely of studies on systems containing non-ionogenic water-soluble polymers. The general laws of the adsorption of polymers and the structure of the electrical double layer have been discussed in greater detail in monographs[3-5] and in textbooks of colloid chemistry.

II. EFFECT OF ADSORPTION OF POLYMERS ON SURFACE CHARGE DENSITY

The surface charge density of dispersed particles is often determined by potentiometric titration or radiometry (by means of radioactive tracers), which have been described in detail[6-9]. In the case of polymer-containing disperse systems determinations have several peculiarities, which must be taken into account in the interpretation of the effect on surface charge density of the adsorption of macromolecular compounds[1,2].

If polymer macromolecules are adsorbed on particles of a suspension or a sol, there are grounds for supposing that the surface of the dispersed phase accessible to adsorption of macromolecules will differ from the surface available for the adsorption of potential-determining ions. Quantitative aspects of this effect depend on the nature of the dispersed phase and the added polymer, and perhaps on the sequence in which the components are mixed, the concentration of the dispersed particles, and their size. However, in most cases it must be expected that a smaller surface will be accessible to macromolecules than to ions, because the internal surface of narrow pores cannot be reached by macromolecules, and also because of aggregation of particles. The latter factor is responsible for the well known decrease in adsorption of polymers with increase in concentration of the dispersed phase[10,11]. Investigations of the adsorption of polyvinyl alcohol, potential-determining ions, and dyes on particle surfaces in suspensions and sols of silver iodide have shown[1,2,12] that, under otherwise similar conditions, particles of a suspension adsorb a smaller quantity of polymer than do those of a sol, and that in suspensions 35% of the surface is unavailable for polymer adsorption.

It follows from the above that, for dispersions containing added polymers, the observed surface charge density is a composite, "mixed" quantity, somewhere between the value in the absence of an adsorbed layer and the value for portions of the surface modified by adsorption of the polymer. On the assumption that covered and uncovered parts of the surface are independent, we can write[2]

$$\sigma_{av} = f\sigma(\theta) + (1-f)\sigma_0, \qquad (1)$$

where f is the portion of the surface of charge density $\sigma(\theta)$ modified by adsorption, $1-f$ is the portion of unmodified charge density σ_0 and θ is the coverage of the surface by monomer units of adsorbed macromolecules. If f and σ_0 are known, relation (1) can be used to determine $\sigma(\theta)$. Lack of information on the accessibility of the surface to macromolecules may be a source of error in calculations of the parameters of adsorbed layers. Up to the present an aqueous dispersion of silver iodide containing polyvinyl chloride is the only system for which such information has been obtained from systematic investigations[1,2,12].

Another peculiarity is that the observed value σ_{av} is an average parameter, since the adsorption properties are different at different sites on the surface, which leads to inhomogeneity of the adsorbed layer. Combined surface electrical measurements do not yet allow more detailed information to be obtained, but this defect is inherent in most other methods of studying the adsorption of polymers.

The third feature is that the adsorption of compounds of high molecular weight, in contrast to that of the lower surface-active compounds, is in many cases irreversible. Yet the thermodynamics of surface phenomena, which is usually employed for the quantitative interpretation of surface electrical measurements, is applicable only to equilibrium reversible processes. Since the adsorption of polymers at the interface between a solid and a liquid solution depends both on the concentration of the polymer and on the parameters of the electrical double layer, two types of reversibility must be distinguished here—with respect to the concentrations of adsorbate and of potential-determining ions (e.g. pAg for silver iodide and pH for oxides).

The adsorption of macromolecular compounds from solution on colloidal particles is usually irreversible with respect to the adsorbate concentration[2], but it may be reversible (to a considerable degree, if not completely) with respect to the concentration of potential-determining ions, and then the dependence of the parameters of the adsorbed layer on the latter concentration can be subjected to thermodynamic analysis[2]. The degree of reversibility can be inferred from special adsorption experiments and also from certain indirect criteria, e.g. the appearance of hysteresis between σ—pAg or σ—pH curves obtained in the presence of the polymer with increasing and with decreasing concentration of potential-determining ions, and from the presence of a common point of intersection of these curves for different polymer concentrations, which will be discussed below. The actual degree of reversibility depends also on the time factor—on the rate of variation of pAg or pH during the experiment.

Before analysing the experimental results, we shall briefly examine theoretical views on the mechanism by which the adsorption of non-ionogenic water-soluble polymers affects the surface charge density of dispersed particles. This effect is usually due to the combined action of several factors (below).

(*a*) *Variation of χ-potential*[13]. The interphase potential difference $\Delta\phi$ established on contact between particles of a dispersed phase and a liquid solution comprises in general[13] two components: the ionic $\Delta\phi_i$ is due to the presence of an ionic double layer at the interface; and the dipolar χ is caused by the orientation of solvent (water) molecular dipoles in the vicinity of the interface. If adsorption of a polymer is accompanied by orientation of dipolar units of the macromolecules near the adsorbent surface, such orientation will lead to an additional interphase potential difference $\Delta\phi_a$, depending in magnitude and sign on the number and polarity of the monomer units, on the character and the degree of their orientation, and also on the degree of displacement of water molecules from the layer adjacent to the surface. Since for a reversible interface the interphase potential difference is determined unambiguously by the activity of potential-determining ions in the solution[14],

the appearance of $\Delta\phi_a$ will be accompanied by a change in the ionic component $\Delta\phi_i$ and hence† by a change in surface charge density, which may either increase or decrease depending on the relation between the signs of $\Delta\phi_i$ and $\Delta\phi_a$. The change in χ due to $\Delta\phi_a$ has been termed the "adsorption potential difference" and has been successfully invoked to explain several colloid-chemical phenomena[1,2,7,15–20] (see below).

(*b*) *Competition with potential-determining ions.* In each of the above cases the surface charge density varies owing to adsorption (desorption) of some of the potential-determining ions. The displacement of their adsorption equilibrium should be especially marked if they and the adsorbate are adsorbed on the same adsorption centres. The effect is not identical with the "adsorption potential difference", since it is purely statistical and is due to the fact that some of the surface centres suitable for adsorption of the ions are occupied by the adsorbate. Thus, if adsorption of the polymer is due to formation of hydrogen bonds with surface acid-base centres (e.g. hydroxy-groups), the adsorbate may compete with other hydrogen or hydroxide ions depending on the zero-charge point of the oxide and the pH of the solution. At sufficiently low pH, at which a considerable proportion of surface hydroxyls are attached to protons, formation of an adsorption bond is difficult and would be accompanied by displacement of some of the hydrogen ions from the surface. With rise in pH the number of free surface hydroxyls will increase, and competition with hydrogen ions weaken; in this pH range the formation of adsorption bonds with polymer macromolecules is facilitated. Finally, at still higher pH decrease in the total number of undissociated surface hydroxyls will lead to competition with hydroxide ions and will hinder adsorption of the polymer; as a result of competition with potential-determining ions the surface charge density diminishes.

(*c*) *Competition with gegenions in the Stern layer.* If the energies of adsorption of units of a polymer chain and of gegenions in the Stern layer are comparable, adsorption of the polymer may involve displacement of gegenions from this layer into the diffuse region of the double layer. This is equivalent to an increase in thickness of the double layer and, provided that the interphase potential difference is constant, should lead to a decrease in surface charge density, i.e. to desorption of some of the potential-determining ions. This mechanism was suggested[21] to explain the decrease in surface charge density on silver iodide as a result of the adsorption of lower aliphatic alcohols, and then was transferred to the adsorption of polymers[1,16]. The influence of competition in the Stern layer on surface charge density may be expected to depend on the density of charges in this layer and hence on the ionic strength of the solution. Yet good agreement has been observed[1] between results obtained in solutions of high and low ionic strength. On the other hand, the adsorption of heptan-1-ol on silver iodide is accompanied by desorption of potential-determining (and silver and iodide) ions only in the presence of a supporting electrolyte[22]. This suggests that the observed effect is a consequence of competition in the Stern layer, not of competition between alcohol molecules and potential-determining ions, as has been assumed[22]. Furthermore, it is difficult to imagine competition between neutral molecules and these ions, especially for adsorption centres on the surface of an ionic crystal.

(*d*) *Variation in distribution of gegenions in diffuse region of double layer.* Although several investigators of polymer-containing disperse systems have suggested that adsorption of the polymer does not affect the distribution of gegenions in the diffuse region of the double layer[6,17,20,23–25], it can reasonably be assumed that this does not apply at sufficiently high surface coverage. For the adsorption of flexible macromolecules on a surface of constant charge density Brooks[26] suggested a model in which the distribution of gegenions was affected by the excluded volume (this model will be examined in greater detail in Section III,1). Provided that the interphase potential difference is constant, the excluded-volume effect should be accompanied by a decrease in surface charge density.

(*e*) *Variation in dielectric constant of surface layer of liquid.* If the dielectric constants of the adsorbate and of water are different, that of the layer adjacent to the surface will change as it becomes enriched with adsorbed macromolecules, with consequent changes in capacitance of the double layer and, the interphase potential difference remaining constant, in surface charge density (for the diffuse ionic double layer $\sigma \propto \varepsilon^{\frac{1}{2}}$).

The relative contribution by each of the above factors to the total change in surface charge density depends on the nature of adsorbate and adsorbent, on the surface coverage and structure of the adsorbed layer, and also on the concentration of potential-determining ions, the composition, and the ionic strength of the solution. At the zero-charge point, of course, where the ionic double layer is absent, factors (*b*)–(*d*) are inoperative, for they are associated with the effect of the polymer on the structure of this layer. With increase in the ionic strength of the solution factor (*c*) should become stronger, and (*d*) weaker. In addition to the above factors we must consider the possibility that the activity coefficients of the ions may vary in polymer solutions, and also that the adsorption of macroions of pseudopolyelectrolytes, whose formation has been suggested by several workers[27,28] for non-ionogenic polymers in concentrated solutions of salts.

The displacement of the adsorption equilibrium of potential-determining ions on the adsorption of a polymer will lead to a more or less considerable change in their activity in solution, so that a cautious approach must be made to the principle of constancy of the interphase potential difference. Furthermore, the above theoretical analysis suggests that the adsorption of polymers and that of simple surface-active compounds have largely similar effects on the surface charge density.

Most of the experimental work on the effect of the adsorption of polymers on surface charge density has been done on classical hydrophobic dispersions of silver iodide or of metal sulphides, as well as on dispersions of oxides.

Silver iodide

The interface between silver iodide and an aqueous solution is one of the most thoroughly studied by colloid-chemical methods, so that it is not surprising that the effect of the

†It is assumed that, with the exception of the cases specially mentioned, the potential difference between the surface and a point inside a solid phase is constant. Variations in $\Delta\phi_i$ may then be identified with those in the surface potential ψ_0.

adsorption of non-ionogenic water-soluble polymers on the surface charge density of colloidal particles was first investigated precisely on aqueous dispersions of silver iodide. Lyklema and his coworkers[1,2,6,12,29] have used potentiometric titration to study the effect of the adsorption from aqueous solution of several specimens of polyvinyl alcohol, differing in molecular mass and in acetate-group content, on the surface charge density of silver iodide particles. The typical σ–pAg relations illustrated in Fig. 2 show that (i) the adsorption of polyvinyl alcohol diminishes the slope of the curves, (ii) the zero-charge point is displaced to more positive values, and (iii) all the curves pass through a common point of intersection. The effect produced depends on the characteristics of the specimen of polyvinyl alcohol used: it is stronger for a polymer containing 12% of acetate groups than for one containing 2%.

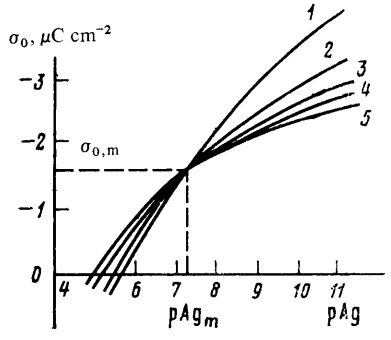


Figure 2. Surface charge density of silver iodide particles in presence of adsorbed pva of mol.wt.106500 in 0.1 M KNO_3 for various quantities of polymer adsorbed[2,12] (mg m^{-2}): *1*) 0; *2*) 0.05; *3*) 0.18; *4*) 0.38; *5*) 0.4.

The decrease in slope of the σ–pAg curves is equivalent to a decrease in the differential capacitance of the double layer, and should be attributed[1] to two main factors—displacement of the originally specifically adsorbed gegenions by monomer units of the polymer, and decrease in the dielectric constant of the layer adjacent to the surface by replacement of water molecules by units of the polymer chain, i.e. the above factors (*c*) and (*e*).

The shift in the zero-charge point may be due to change in the specific adsorption of ions, the activity coefficient of potential-determining ions, or the electrokinetic potential when water dipoles in the surface layer are replaced by the dipoles of polymer units. The last factor probably predominates, since the change in the activity coefficient appears[1] to be negligible, while the specific adsorption of nitrate ions is insignificant at the zero-charge point. The observed shift was explained[1,2,12] in terms of ideas developed earlier[7,15,30] in relation to the adsorption of simple compounds on silver and mercury iodides. The important conclusion was reached that electrochemically the adsorption of polyvinyl alcohol has much in common with that of simple compounds, and that a layer of the polymer adsorbed on the surface of silver iodide can be regarded as comprising 50% of butanol and 50% of ethylene glycol molecules. Such an approach enabled the proportion of occupied sites in the first dense layer of adsorbate to be calculated (see below for greater detail).

A common point of intersection has been observed also in the adsorption of substances of low molecular weight on silver and mercury iodides[7,30]. Examination of the Gibbs adsorption equation shows that the point of intersection then corresponded to the surface charge density at which maximum surface excess of adsorbate relative to water occurred[2,7]. The existence of a common point of intersection of σ–pAg curves in the adsorption of a polymer suggests that the adsorption of monomer units directly in contact with the surface is reversible with respect to pAg, at least if changes in pAg are not too large. At σ_m the maximum number of units are in contact with the surface, and the θ–σ relation, in effect the θ–pAg relation, can be subjected to thermodynamic analysis, even if the total polymer adsorption is irreversible with respect to concentration[2]. The position of σ_m depends on the nature of adsorbate and absorbent and on the composition of the solution[1,2,12]; it is characteristic of the system, independently of the total polymer adsorption. For silver iodide $\sigma_m = -1.6$ and -2.2 μC cm^{-2} in aqueous solutions of polyvinyl alcohols pva-2 and pva-12 with potassium nitrate as inert electrolyte (here and subsequently the numerals denote the contents (%) of unsaponified acetate groups in the polymer)[1,12]. The value obtained for the "50% butanol + 50% ethylene glycol" model was $\sigma_m = -1.7$ μC cm^{-2}, in good agreement with the experimental value for pva-2.[1] The differences observed in the electrochemical behaviour of pva-2 and pva-12 were not explained[1].

The effect of the adsorption of polyvinyl alcohol and another non-ionogenic polymer—polyethylene oxide (peo)—from aqueous solution on the surface charge density of silver iodide has been investigated by a radioactive tracer method[17–19,24,31]. The silver iodide surface was labelled with radioactive iodine-131 by isotopic exchange, and the variation in the adsorption of potential-determining iodide ions was assessed from the radioactivity of the liquid after 24-h contact of the radioactive precipitate with solutions of the polymers varying in molecular mass. The results indicate that under the experimental conditions adsorption of the polymers on a negatively charged precipitate of silver iodide is not accompanied (as in the case of non-ionogenic surface-active agents[32]) by desorption of potential-determining iodide ions.

Ideas on the "adsorption potential difference" were successively applied to explain the influence of the adsorption of polyethylene oxide on the surface charge density and the electrokinetic potential of colloidal precipitates[16–20,33]. It was concluded that, during adsorption on silver iodide particles, $\Delta\phi_a$ and $\Delta\phi_i$ are opposite in sign at negative surface charge densities, and of the same sign at positive values of the latter. Hence dipolar units of adsorbed macromolecules in contact with the surface are oriented with the negative pole (i.e. the oxygen atom) towards the liquid phase, independently of the sign of the surface charge, in agreement with other results[34]. The positive shift in the surface potential of a mercury electrode in solutions of polyethylene oxide has also been explained[35] by the adsorption of oriented dipoles. However, without additional information on the degree of displacement of water from the layer adjacent to the surface and on the polarity of the adsorbate, or on the character of the bond between polymer and surface, the sign of $\Delta\phi_a$ cannot be regarded as evidence of a particular orientation of the adsorbed units.

Antimony sulphide

Results have been published also on the influence of polyvinyl alcohol and polyethylene oxide on the surface charge density of antimony sesquisulphide[17-19,23,24]. Variation in the latter was assessed from that of the total absorption of calcium gegenions from solutions of the chloride or nitrate labelled with calcium-45, at electrolyte concentrations ensuring that the adsorption isotherms of the gegenions reached saturation.

The results of radiometric and adsorption measurements in Table 1 indicate a significant difference between antimony sulphide and silver iodide particles in their surface interaction with polyethylene oxide. With increase in adsorption of the polymer the surface charge density of the sulphide falls to a certain level, after which it remains unchanged. It is significant that this decrease, for a given quantity adsorbed, is independent of the molecular mass of the polymer.

Table 1. Adsorption of peo and Ca^{2+} from aqueous solution on Sb_2S_3 particles[19].

[peo], g litre^{-1}	$M_{peo} = 6000$		$M_{peo} = 1\,300\,000$	
	[peo], mg g^{-1}	[Ca^{2+}], μg-equiv. g^{-1}	[peo], mg g^{-1}	[Ca^{2+}], μg-equiv. g^{-1}
0	0	42.0	0	42.0
0.1	5	38.9	5	38.5
0.3	15	35.8	15	36.4
1.0	—	35.2	38	36.4
2.5	37	35.2	55	36.4

The decrease in the surface charge density of the sulphide accompanying adsorption of polyethylene oxide was regarded[17-19] as indicating that $\Delta\phi_a$ and $\Delta\phi_i$ had the same sign. Since the sulphide surface is negatively charged in water, $\Delta\phi_a$ must have a minus sign. This suggests that the orientation of monomer units is opposite to that on silver iodide, and has the oxygen atom towards the surface[19]. Such orientation may result from hydrogen bonding between oxyethylene oxygen and hydrogen of acidic groups on the sulphide surface, as infrared spectroscopy has established[36] for the aqueous silica-polyethylene oxide system. The decrease in negative values of $\Delta\phi_i$ (and ψ_0) due to such orientation should be accompanied by a decrease in the surface charge density of the antimony sulphide particles, as has been observed. Hence the statement[32] that the orientation of dipolar molecules adsorbed from aqueous solution is independent of the nature of the surface is hardly applicable to the specific interaction of adsorbate molecules with the surface of dispersed particles.

In contrast to polyethylene oxide, pva-2 and pva-12 added to an electrolyte solution up to a polymer concentration of 0.75 g litre^{-1} hardly affect the absorption of calcium genenions[23]: i.e. the surface charge density of antimony sulphide remains unchanged in the presence of adsorbed polyvinyl alcohol. This makes it highly probable that the number of monomer units of adsorbed macromolecules in contact with the sulphide surface is small: i.e. certain qualitative deductions can be made concerning the structure of an adsorbed polymer layer.

Oxides

Though polymer-containing dispersions of inorganic oxides have the greatest practical value among all the systems examined, their study began only during recent years and has been predominantly incidental. The hydrophilic character of oxide surfaces, the presence on them of functional hydroxy-groups, and characteristic structural features of the electrical double layer (the existence of a porous gel-like layer, permeable to potential-determining ions and gegenions, on the surface of certain oxides[37-40]) distinguish oxide dispersions as a special independent group of systems, whose study is of both theoretical and practical interest.

All results published at the present time have been obtained by potentiometric titration of polyvinyl alcohol–oxide systems. Adsorption of the polymer affects neither the position of the zero-charge point nor the surface charge density of haematite[2], gibbsite[41], and amorphous silica (Aerosil)[42]. The explanation for iron(III) and aluminium oxide was[2] that their surface charge was not concentrated at the surface but spread inside the superficial (gel-like) layer of solid, and this region of the electrical double layer was "invisible" to the polymer. In the Reviewers' opinion the reason may be "spreading" of the Stern layer owing to diffusion of gegenions inside the gel, which under the conditions of a potentiometric titration (solution of high ionic strength) should diminish the influence on surface charge density of competition in this layer. Furthermore, the effects of polymer adsorption on surface charge density outlined above may in considerable measure all be levelled off by the redistribution of charges and potentials in the gel-like layer, so that the change in surface charge density represents only an insignificant part, difficult to detect experimentally, of the total change in space charge.

Potentiometric titration of suspensions of Aerosil in the presence of polyvinyl alcohol has been undertaken at both high and low ionic strengths[42,43]. Since a gel-like layer is not present at the surface of Aerosil particles[44], the insensitivity of surface charge density to polymer adsorption is obviously due in this case to the insignificant number of contacts between adsorbed macromolecules and adsorbent surface.

Although potentiometric titration has not given positive results in relation to the adsorption of polyvinyl alcohol on iron(III) and aluminium oxides, the view[2] that this method is inapplicable to polymer-containing oxide dispersions can be accepted only for oxides whose surface is coated with a gel-like layer. But even in this case we cannot speak in advance of the inapplicability of potentiometric titration, since, with adsorbed macromolecules having a sufficiently strong influence on the structure of the electrical double layer, a change in surface charge density might nevertheless be detected. Finally, the surface charge density of zinc oxide is affected significantly by the adsorption of polyvinyl alcohol[45], with displacement of the zero-charge point of the oxide to higher pH. This should be regarded as indirect evidence of absence of a gel-like layer from the surface of zinc oxide, but the results[45] indicate a considerable number of polymer chain units in contact with the surface.

Thus even with dispersions of oxides study of the influence of the adsorption of polymers on surface charge density can give valuable information. Nevertheless, the above survey shows that the range of systems studied by this method is narrow, and further research on these lines is extremely desirable.

III. ADSORPTION OF POLYMERS AND ELECTROKINETIC POTENTIAL OF DISPERSED PARTICLES

The adsorption of polymers may lead to changes not only in surface charge density but also in magnitude and sometimes even sign of the electrokinetic potential. Results obtained in the study of these properties of disperse systems supplement each other.

The combined action of three factors—change in potential of the outer Helmholtz plane ψ_δ, displacement of the plane (more precisely region) of slippage within the liquid phase as a consequence of the formation of a sufficiently thick adsorbed layer on the adsorbent surface, and change in the distribution of gegenions in the diffuse region of the electrical double layer—is able to explain the influence of adsorption of a non-ionogenic polymer on the electrokinetic potential. The first of these obviously predominates at low surface coverage, and the second when adsorption is sufficiently great; the only attempt to use the third factor to explain experimental results is the Brooks model discussed below.

Changes in ψ_δ are in most cases due to corresponding changes in $\Delta\phi_i$, ψ_0, and σ (see footnote in Section II), so that a theoretical interpretation of the influence of polymer adsorption on electrokinetic potential involves discussion of its above effects on surface charge density. This potential may either increase, decrease, or change sign as a consequence of changes in ψ_δ. Displacement of the slippage plane into the solution is accompanied solely by a decrease in the electrokinetic potential and depends on the thickness of the adsorbed layer and the degree of immobilisation of liquid in it. The relative contributions by each of these factors to the resultant change in potential depends on the same characteristics of the system as does the change in surface charge density (Section II), in particular on the quantity of polymer adsorbed, and the structure and thickness of the adsorbed layer. With the exception of quantity adsorbed, direct experimental determination of these characteristics is not possible. Since they are related to such parameters of the system as the concentrations of polymer and potential-determining ions, and the composition and ionic strength of the solution, the immediate task of experimental study of the electrokinetic behaviour of polymer-containing disperse systems is to establish the dependence of the electrokinetic potential on these parameters.

1. Dependence on Polymer Concentration

Electrokinetic results are most often presented as ζ–c curves, where c is the equilibrium or initial polymer concentration. Fig. 3 shows the dependence of the electrokinetic potential of the particles in silver iodide and antimony sulphide sols on the concentrations of added polyvinyl alcohol and polyethylene oxide solutions[24]. Increase in the polymer content of the system is accompanied by a continuous

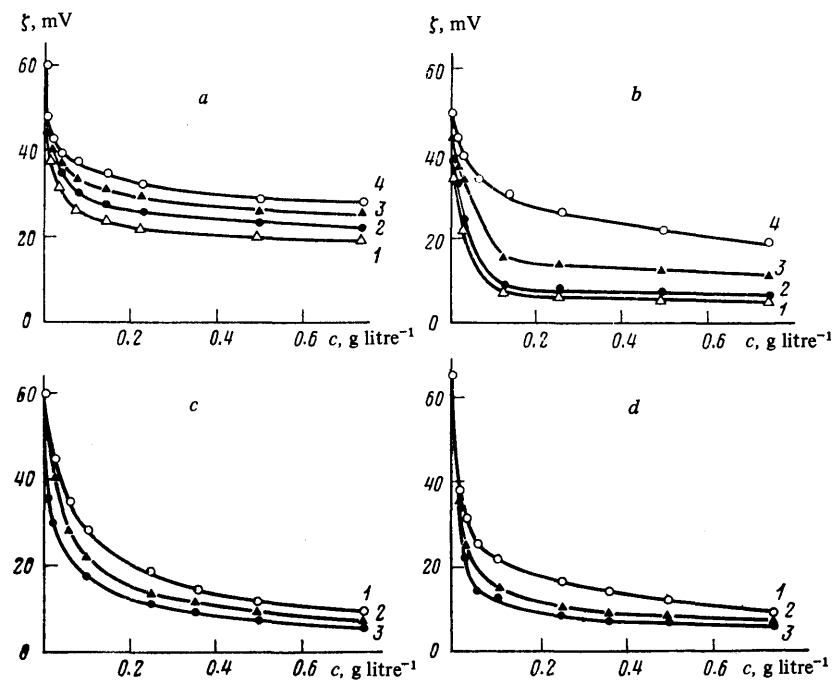


Figure 3. Effects on the electrokinetic potential of sol particles of (*a*) AgI and (*b*) Sb_2S_3 of the addition[24] of polyvinyl alcohols varying in molecular mass (10^{-4} *M*): *1*) pva-12 (2.2); *2*) pva-2 (4.1); *3*) pva-12 (5.9); *4*) pva-18 (6.5); and for (*c*) AgI and (*d*) Sb_2S_3 of the addition of polyethylene oxides (10^{-6} *M*): *1'*) 0.23; *2'*) 1.3; *3'*) 2.6.

decrease in the potential. The main fall usually occurs with small additions of polymer, after which the curves become more gently sloping, with a tendency to emerge on a plateau. Similar curves have been observed in the adsorption of these polymers on silica[16,42], negatively charged precipitates of silver iodide and antimony(III) sulphide[20,24,33], and aluminium oxide[41].

Such variation in the electrokinetic potential indicates the dominant effect of displacement of the slippage plane, some decrease in ψ_δ, or parallel action of the two factors. Since the adsorption of polyethylene oxide and polyvinyl alcohol on silver iodide and of the latter on antimony(III) sulphide particles is not accompanied by decrease in the negative surface charge density (above), the decrease in the negative electrokinetic potentials is due to the dominant effect of displacement of the slippage plane inside the solution. The fall in potential in the antimony sulphide–polyethylene oxide system is due to the combined action of the two factors, since adsorption of this polymer on the sulphide surface leads to some decrease in surface charge density. Finally, the latter remains unchanged during the adsorption of polyvinyl alcohol on silica[42] and gibbsite[41], so that the fall in potential can be attributed solely to the formation of quite thick adsorbed polymer films on these precipitates.

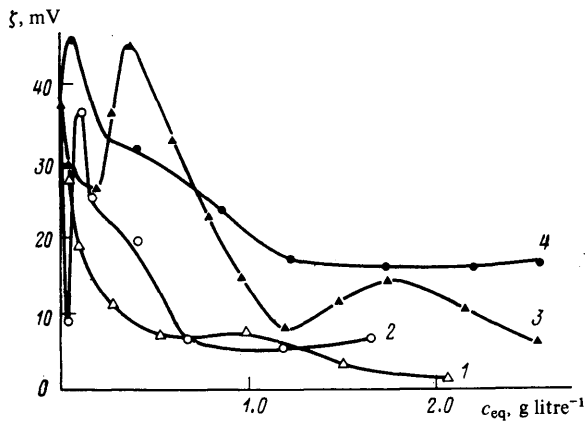


Figure 4. Dependence of electrokinetic potential of zinc oxide particles on equilibrium solution concentration[46] of polyvinyl alcohols (10^{-4} *M*): *1*) pva-12 (5.0); *2*) pva-2 (5.6); *3*) pva-18 (5.9); *4*) pva-18 (9.8).

If the above two factors have opposite effects, while the increase in ψ_δ predominates in a certain polymer concentration range, extrema appear on the ζ–*c* curves. Fig. 4 illustrates this relationship for zinc oxide in aqueous solutions of four specimens of polyvinyl alcohol[46] having different contents of acetate groups. The surface charge density of the oxide becomes more positive in solutions of pva-2 ($M = 56000$),[45] which is equivalent to increases in $\Delta\phi_i$ and ψ_δ for a positively charged surface, and should tend to raise a positive electrokinetic potential. Quantitatively this effect and also the thickness of the adsorbed polymer layer depend on the specimen of polyvinyl alcohol used.

When the increase in ψ_δ is sufficiently large, a maximum appears on the ζ–*c* curves in the corresponding concentration range (curves *2*–*4*). Among all the specimens studied[46] pva-12 gives the greatest adsorption, and forms a thick adsorbed layer even at low concentrations, which leads to a sharp drop in potential (curve *1*) and "masks" the effect of the increase in ψ_δ. Analogous ζ–*c* relations are observed on silica[42], although adsorption of polyvinyl alcohol does not affect the surface charge density[42]. Thus the presence of extrema in the curves should not by itself be regarded as evidence of change in σ, $\Delta\phi_i$, or ψ_0.

The form of the curves depends substantially on the magnitude and sign of the surface charge, i.e. on the concentration of potential-determining ions. Fig. 5 shows ζ–*c* curves for a precipitate of silver iodide in polyethylene oxide solutions with different contents of non-inert electrolytes[18,20,31]. At low polymer concentrations some increase is observed in the electrokinetic potential of a negatively charged surface and a sharp drop in potential of a positively charged precipitate (to zero), change in sign of charge, and rise in potential of opposite sign.

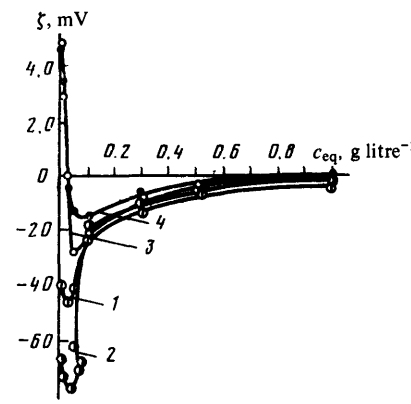


Figure 5. Dependence[17,20] of electrokinetic potential of silver iodide particles on concentration of polyethylene oxide (molecular mass 1.05×10^6) in: *1*) water; *2*) 0.1mM KI; *3*) 0.5mM $AgNO_3$; *4*) 1mM $AgNO_3$.

Change in sign on a positively charged surface of silver iodide in solutions of polyethylene oxide, observed also[34] in the coagulation by electrolytes of silver iodide sols stabilised by this polymer, has been explained[18,20,31] by the establishment of a considerable "adsorption potential difference" when the polymer is adsorbed on silver iodide particles. As noted above, with $\Delta\phi_a$ and $\Delta\phi$ having the same sign, $\Delta\phi_i$ should decrease when $\Delta\phi$ is constant. If the difference $\Delta\phi_a$ is sufficiently large ($\Delta\phi_a > \Delta\phi_i$), its compensation may require change not only in the absolute magnitude but also in the sign of $\Delta\phi_i$, which is evident in electrokinetic measurements as a change in sign of the ζ-potential.

If it is assumed, as for the interface between mercury and aqueous polyethylene oxide[35], that dipolar units of the polymer chain are oriented with their positive poles towards

the hydrophobic surface of silver iodide (independently of the sign of its charge), the sign of $\Delta\phi_a$ will be the same as or opposite to that of $\Delta\phi$ according as the silver iodide particles are positive or negative. This should lead to an increase in negative values of $\Delta\phi_i$, ψ_δ, and hence the electrokinetic potential, as well as a decrease and change in sign of positive $\Delta\phi_i$ and ζ, as is observed experimentally. With increase in concentration of polyethylene oxide the ζ-potential falls, independently of the sign of the particle charge, as a result of formation of a thick adsorbed polymer film and displacement of the slippage plane deep into the solution.

As already noted, we have explained the changes in the electrokinetic potential of hydrophobic silver iodide and antimony sulphide surfaces in aqueous solutions of polyethylene oxide and polyvinyl alcohol mainly[16-18,20,33] in terms of an "adsorption potential difference", since this is the only factor explaining the change in sign of the surface charge accompanying polymer adsorption. Yet changes in ψ_δ and hence the ζ-potential may be due also to competition between dipolar units of adsorbed macromolecules and gegenions in the dense region of the electrical double layer. Since such competition leads to a decrease in surface charge density (above), it may cause decreases in ψ_0, ψ_δ, and ζ. On the other hand, diminution in the charge density of gegenions in the dense region may be accompanied by increases in ψ_δ- and ζ-potentials, even with a general decrease in surface charge density. These ideas have been used to explain the influence of added alcohols on the stability of aqueous dispersions of silver iodide[21], but in published studies of adsorbed layers of macromolecular compounds they receive only casual mention[2].

Although most authors, when analysing electrokinetic measurements regard the interphase potential difference as unchanged for a given activity of potential-determining ions in the solution, attempts have also been made to use a constant-charge model. When studying the electrokinetic potentials of erythrocytes, quartz, and latices in aqueous salt solutions of dextran and polyethylene glycol, Brooks[47,48] observed a rise in this potential with increase in the polymer concentration. He explained and gave a quantitative basis to these results on the hypothesis that the excluded-volume effect arising within the electrical double layer on adsorption of a polymer leads to expansion of the diffuse region of the layer and a rise in the surface potential with the surface charge density unchanged[26]. If the displacement of the slippage plane is not too great, the electrokinetic potential rises also, and this plane may even lie within the adsorbed polymers layer[26]. This model is obviously not generally applicable, since the adsorption of non-ionogenic polymers may be accompanied not only by a rise but also by a sharp drop in the electrokinetic potential, even with little adsorption, when it is difficult to expect significant movement of the slippage plane. Furthermore, other reasons for a rise in electrokinetic potential are possible, although the excluded-volume effect probably also makes a definite contribution. The Brooks theory has been subjected to critical analysis[2].

2. Dependence on Adsorbed Quantity of Polymer

Adsorption and electrokinetic measurements on the same systems will give the dependence of ζ-potential on polymer adsorption, which Fig. 6 illustrates for particles of silver iodide and antimony(III) sulphide sols coated with adsorbed polyvinyl alcohol or polyethylene oxide[24]. In general these

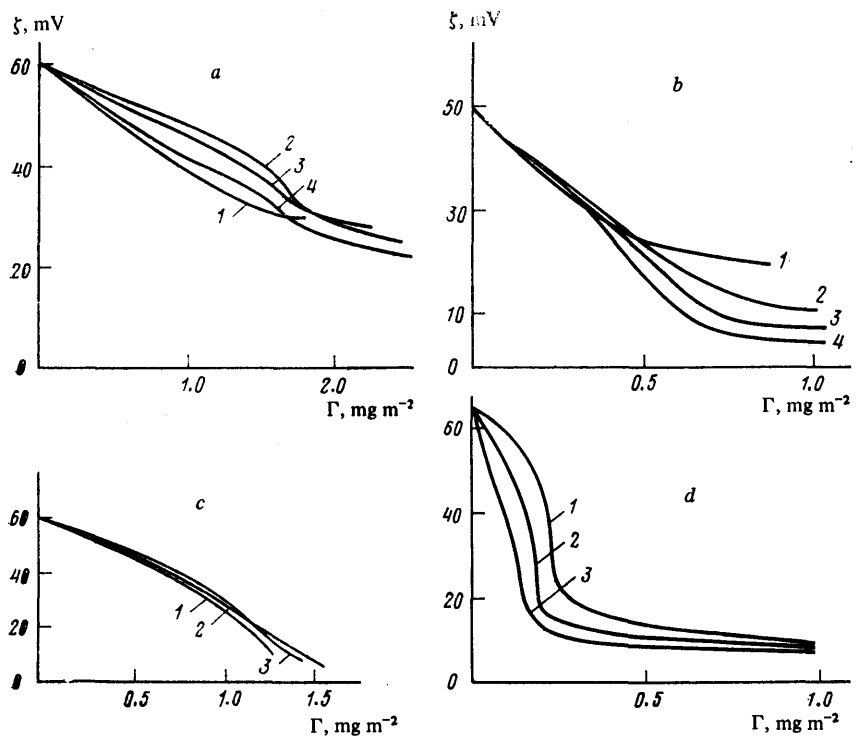


Figure 6. Variation[24] of ζ-potential of sol particles with quantity of adsorbed polymer: *a*) pva on AgI; *b*) pva on Sb_2S_3; *c*) peo on AgI; *d*) peo on Sb_2S_3. Numbering of curves as in Fig. 3.

curves resemble those for the dependence of the potential on the quantity of added polymer (Fig.3), but with the difference that increase in polymer adsorption is accompanied by an initial slow fall in electrokinetic potential followed by a more rapid drop, which is replaced by another gradual decrease, after which in many cases a plateau ensues. Since the fall in ζ-potential on the adsorption of polyvinyl alcohol on silver iodide and antimony sulphide surfaces, and of polyethylene oxide on the former, is due to displacement of the slippage plane from its original position, a ready explanation for the initial slow decrease is that the early portions of the polymer, which form a thin adsorbed layer comparable in thickness with the Stern layer, are unable to produce a significant drop in potential by this mechanism. After the first (dense) layer has been formed, further accumulation of macromolecular compound at the surface of the dispersed phase is due to lengthening of loops and spikes of adsorbed macromolecules, i.e. to thickening of the layer.

If the slippage plane is assumed to have moved to or at least near the boundary of the polymer envelope, the observed sharp drop in electrokinetic potential can reasonably be attributed to formation of the adsorbed layer, a process whose termination is indicated by emergence of the curves on a plateau (Fig.6). The sharper drop in the potential at low surface coverage of the antimony sulphide precipitate with polyethylene oxide[17,18,31] is due to the accompanying decrease in surface charge density. Good correlation has been noted[16] also in the influence of the molecular mass of polyethylene oxide on the electrokinetic potential of quartz immersed in its solutions and on the limiting adsorption of the polymer on Aerosil.

3. Dependence on Concentration of Potential-determining Ions

The influence of the concentration of potential-determining ions on the electrokinetic potential of polymer-containing disperse systems has been studied[1,2,6,12,49], and results obtained for quartz in aqueous solutions of polyethylene oxide are illustrated in Fig.7.[49] This polymer lowers substantially the ζ-potential of quartz in acid and weakly alkaline pH ranges, the decrease at constant pH being little dependent on the polymer concentration, for adsorption saturation of the quartz surface is already reached at low concentrations. With rise in pH above 9.5 the effect of the polymer on the potential diminishes, which is consistent with the decrease in adsorption of the polymer on amorphous silica (Aerosil) with rise in pH.

Such diminished effect suggests competition between hydroxide ions and polyethylene oxide for acidic adsorption centres on the surface, as well as certain conclusions on the nature of the bond between polymer and adsorbent surface. These deductions are supported by infrared spectral results[36], indicating hydrogen bonding between oxygen atoms in the polymer chain and undissociated silanol groups of the silica surface. As a consequence of this competition the pH values of maximum electrokinetic potential shift to a more alkaline range. It is significant that this maximum is about the same for all the curves and is independent of the presence of polyethylene oxide. This was regarded[49] as unambiguous evidence that at pH ≥ 11 the number of vacant undissociated adsorption centres is too small to ensure adsorption of the polymer.

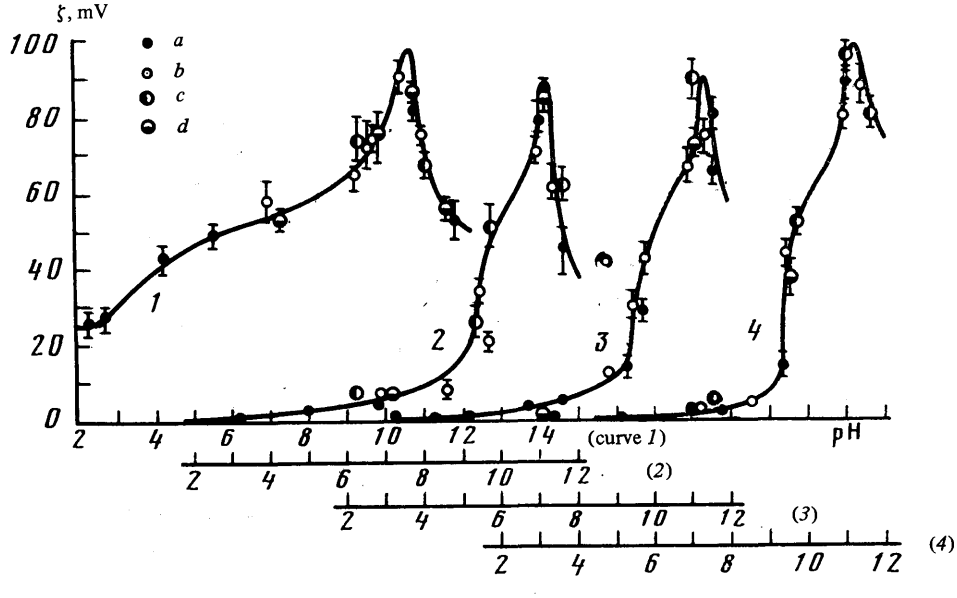


Figure 7. Dependence[49] of ζ-potential of quartz on pH for different concentrations of polyethylene oxide (g litre^{-1}); *1*) 0; *2*) 0.1; *3*) 0.3; *4*) 0.5 in: *a*) HCl; *b*) LiOH; *c*) NaOH; *d*) KOH.

The electrophoretic particle mobility of silver iodide sols in the presence of polyvinyl alcohol has been measured[1,2,6,12] as a function of pAg (Fig.8). Adsorption of the polymer is accompanied by a shift in the isoelectric point to more positive values, decrease in mobility in the region of a plateau, and diminished slope of the curves at this point. The shift in the point has been attributed[1,2,12] to displacement of dipolar water molecules from the surface layer by units of adsorbed macromolecules. The most marked shift in isoelectric point occurs with the initial portions of adsorbed polymer, which complete mainly a compact layer in contact with the particle surface. Subsequent portions are adsorbed predominantly by the lengthening of loops and spikes of adsorbed macromolecules, and the shift gradually reaches saturation. The lowering of the electrokinetic potential in the region of the "plateau" (Fig.8) and the decrease in slope of the curves at the isoelectric point are explained by movement of the slippage plane deep inside the solution on adsorption of the polymer. The shift in the isoelectric point and the diminution in slope have been used[1,2,12] to calculate certain parameters of adsorbed layers of polyvinyl alcohol on the surface of silver iodide particles (Section IV).

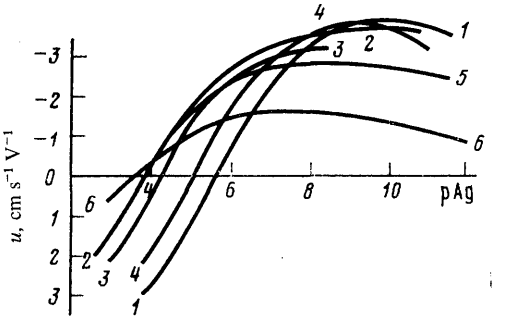


Figure 8. Dependence of electrophoretic mobility of particles of AgI sol in lmM KNO_3 on pAg in presence of different quantities (mg m^{-2}) of adsorbed pva-2 ($M = 106500$): *1*) 0; *2*) 0.12; *3*) 0.37; *4*) 0.50; *5*) 0.75; *6*) 1.00.

4. Dependence on Ionic Strength of Solution

Published information on the influence of ionic strength on the electrokinetic potential of particles in polymer-containing dispersions is extremely limited. Research[43,46,50] has actually been devoted to the effect of added inert electrolytes on the ζ–c relation. The changes observed with increase in ionic strength are explained by the effect of the added electrolyte on the thermodynamic character of the solvent, the quantity of polymer adsorbed, and the structure of adsorbed and electrical double layers. The adsorbed polymer sheath is regarded[51] as becoming increasingly permeable hydrodynamically with increase in the ionic strength of sufficiently concentrated electrolyte solutions, with a consequent displacement of the slippage plane into the adsorbed layer, approaching ever closer to the solid surface.

IV. EFFECT OF ADSORPTION OF POLYMERS ON CONDUCTIVITY OF DISPERSIONS

The electrokinetic charge σ_s usually constitutes only a small fraction of the charge in the outer part of the double layer of colloidal particles. The surface charge is in general balanced not only by the electrokinetic charge but also by gegenions present in the Stern layer and also—in the presence of a hydrodynamically stationary boundary liquid layer[52–54] or a gel-like layer (as on oxide surfaces[37–40])—by a mobile charge located in them. Fridrikhsberg et al.[55,56] showed that the mobility of ions in the stationary liquid boundary layer is closely similar to mobilities in bulk. Hence measurements of surface conductance or dielectric constant at low frequencies, which are sensitive to the ionic concentration throughout the diffuse region of the double layer, may give information on the potential ψ_δ at the boundary of the Stern layer. A quantitative theory of such an approach taking into account polarisation of the double layer has been developed by Dukhin et al.[3,4].

Calculation from measured specific surface conductances κ^σ of ψ_δ-potentials in the presence of adsorbed macromolecules is of interest from several points of view. Firstly such results supplement information, obtained from electrokinetic measurements, on the influence of the adsorption on the structure of the electrical double layer of particles. Secondly they help to reveal the mechanism of the stabilising effect of macromolecular compounds on colloidal solutions, whose stability may be determined under certain conditions, even in the presence of an adsorbed polymer layer, by the repulsion of electrical double layers[57,58]. Thirdly the possibilities of investigating the three-dimensional structure of adsorbed layers of non-ionic macromolecules are considerably increased if study of the electrokinetic potential is paralleled by that of the effect of polymer adsorption on specific surface conductance.

Whereas dozens of studies have been published on the surface conductance of dispersed particles (and have been reviewed[3]), the problem of the effect of adsorbed macromolecules on specific surface conductance has merely been posed. One of the Reviewers[59] has examined the influence of the adsorption of polyethylene oxide and polyvinyl alcohol on the conductivity of suspensions of spherical particles of antimony sulphide and polystyrene latex, as well as rod-shaped particles of the mineral palygorskite. The relative conductivity $\bar{K}/K$ of the suspensions ($\bar{K}$ being the conductivity of the suspension and K that of the dispersion medium) varied linearly with volume fraction p of the solid phase in all cases, the slopes of the straight lines diminishing as the electrolyte concentration in the system increased (Fig.9). This is explained by gradual diminution in the contribution to conductivity of surface conductance owing to the increase in conductivity of the dispersion medium and compression of the electrical double layer. With polarisation of the double layer taken into account the dependence of $\bar{K}/K$ on p for spherical and needle-shaped particles is described[3] by the equations

$$\frac{\bar{K}}{K} = 1 + 3p\left[-\frac{1}{2} + \frac{3}{2}\frac{\mathrm{Rel}}{(1+2\mathrm{Rel})}\right], \qquad (2)$$

$$\frac{\bar{K}}{K} = 1 + p\left[-\frac{5}{3} + \frac{2}{3}\mathrm{Rel}\left(1 + \frac{2}{1+2\mathrm{Rel}}\right)\right], \qquad (3)$$

where

$$\mathrm{Rel} = \varkappa^\sigma / Ka, \qquad (4)$$

is a dimensionless parameter[3,60] representing the contribution

by such polarisation to surface electrical phenomena and a is the particle radius. With high electrolyte concentrations, ensuring a negligible contribution by specific surface conductance, the theoretical limiting negative slopes of the dependence of $\overline{K}/K$ on p are realised experimentally, respectively $-\frac{3}{2}$ and $-\frac{5}{3}$ for spherical and needle-shaped particles—formulae (2) and (3).

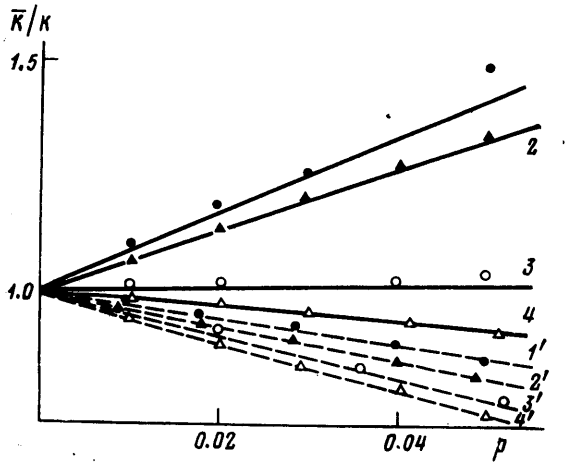


Figure 9. Dependence[59] of relative conductivity of palygorskite suspensions on proportion by volume of solid phase in sodium nitrate solutions of different concentrations (nM): *1*) 0.02; *2*) 0.1; *3*) 0.5; *4*) 5. The primes denote the presence of adsorbed pva-2 of molecular mass 48000.

Adsorption on charged particles of non-ionic polymers leads in all cases (with the electrolyte concentration unchanged) to a diminution in the slope of the relative-conductivity lines, i.e. to a decrease in the conductivity of the dispersion, the effect being larger the greater the quantity of macromolecular compound adsorbed per unit surface (Fig.9). Polymer adsorption may even change the sign of the slope. For example, addition of polyvinyl alcohol (1 mg m^{-2}) to a suspension of antimony(III) sulphide or palygorskite containing 0.01–0.1 M sodium nitrate changes the slope of the dependence of $\overline{K}/K$ on p from positive to negative (Fig.9). Furthermore, adsorption of non-ionogenic polymers gives negative slopes of the straight lines greater in absolute magnitude than would correspond to the limiting theoretical value.

Adsorption measurements[23,61] have shown that under the above experimental conditions all the macromolecular compound introduced into the system is entirely absorbed by the dispersed phase. Therefore surface effects—decrease in cross-section for passage of current in surface layer (which leads to a decrease in κ^σ) and increase in effective particle thickness owing to formation of a thick adsorbed layer—are solely responsible for the observed decrease in $\overline{K}/K$. Both effects cause the parameter Rel to decrease, which theoretically—formulae (2)–(4)—should produce the observed smaller slope of the straight lines. It must be borne in mind that the movement of ions in the adsorbed layer may be hindered not only by monomer units of the macromolecule but also by the few layers of water firmly bound to hydrophilic groups of the polymer, which have lost their solvent power. This view is supported in particular by an investigation by nuclear magnetic resonance of the hydration of polyethylene oxide and polyvinyl alcohol[62,63].

Application of Eqns.(2)–(4) to the results permitted calculation of the specific surface conductance κ^σ and ionic mobility u# within the double layer, as well as their variation in the presence of adsorbed polymer. The calculated values given as example in Table 2 show that increase in polymer adsorption is accompanied by a gradual decrease in κ^σ and u in the double layer, in full agreement with the above qualitative considerations.

Table 2. Effect of adsorption of non-ionic polymers on κ^σ and u of dispersions of palygorskite in 0.1mM $NaNO_3$.[59]

Polymer	10^{-4} M	Γ, mg m^{-2}	$10^9\kappa^\sigma$, ohm^{-1}	u, cm^2 ohm^{-1} g-equiv.$^{-1}$
		—	3.0	5.5
pva-2	4.8	0.3	2.8	5.1
peo	130	0.6	2.2	4.0
pva-23	6.4	0.9	0.9	1.7

The influence of the adsorption of macromolecules on the surface conductance of dispersions has recently been examined theoretically by Dukhin[64] on the view that the structure of the adsorption sheath, like that of a gel[65], can be described by a model of randomly oriented cylinders forming an obstacle to the passage of current. The decrease in the conductivity of a gel K_g relative to that of the electrolyte K is represented[64] by a linear dependence on the volume fraction P_p of the gel (in the present case adsorbed segments of the macromolecule):

$$K_g = K(1 - BP_p). \tag{5}$$

For strongly charged particles ($\tilde{\psi}_\delta = \psi_\delta / kT > 3$–4), provided that change in dielectric constant has little effect on the structure of the double layer, the adsorption P_p of segments diminishes the surface conductance by the factor

$$\beta = \kappa^\sigma(P_p)/\kappa^\sigma(0). \tag{6}$$

The term BP_p can be evaluated from the simplified relation[64]

$$\beta = (1 - BP_p)(1 + 3m)^{-1}, \tag{7}$$

which is valid at high electrolyte concentrations, i.e. when $\kappa h \gg 1$. Here m is a dimensionless parameter representing the contribution to κ^σ by the transport of charges by electro-osmotic flow of the liquid, which can be calculated theoretically, h is the thickness of the adsorbed polymer layer, and κ is the reciprocal of the Debye radius. Thus, by measuring the specific surface conductance in the presence and in the absence of an adsorbed polymer sheath $\kappa^\sigma(p)$ and $\kappa^\sigma(0)$, we can calculate BP_p and then[64] make a choice in favour of a particular dependence of density of adsorbed segments on distance from surface.

More detailed information on the calculation of u will be found in Ref.3.

V. DETERMINATION OF PARAMETERS OF ADSORBED LAYERS OF POLYMERS FROM SURFACE ELECTRICAL MEASUREMENTS

Information on the most important parameters of adsorbed polymer layers—the proportion ν of monomer units in direct contact with the surface, the surface coverage θ by adsorbed units, and the effective thickness h of the adsorbed layer—can be obtained from measurements of surface charge, electrokinetic potential, and surface conductance of particles in the presence of adsorbed macromolecular compounds. Comparison of these parameters with the dimensions of macromolecular coils in solution and with adsorption measurements also leads to definite conclusions on the degree of deformation of macromolecules when adsorbed and on the density distribution of segments along the normal to the surface $\rho(x)$.

Determination of the above characteristics is based on an assumed analogy in structure between the electrical double layer and a surface polymer sheath[1,2,12]. Like the former, which is arbitrarily divided into a dense region (or Stern layer), in which specific interaction takes place between ions and surface, and a diffuse region (Gouy layer) with an exponential fall in concentration of gegenions with distance from the surface, an adsorbed polymer film can be divided into a first (dense) layer of monomer units in direct contact with the surface and a loose layer of spikes and loops directed towards the solution, in which the density of segments gradually diminishes with distance[1]. Many factors—quantity of polymer adsorbed, energy of adsorption of a monomer unit, nature of solvent, flexibility of polymer chain, etc.—determine the nature of the function $\rho(x)$.[5,66-69] The Stern layer and a dense layer of adsorbed units are similar in thickness (~0.4–0.5 nm). Therefore investigation of the former (which is possible in concentrated electrolyte solutions, in which the electrical double layer is strongly compressed) may give information on the parameters of the first layer of units of adsorbed macromolecules, directly attached to the surface. Measurement of the characteristics of the diffuse ionic layer (in dilute electrolyte solutions) gives indications of spikes and loops located beyond the dense layer, the thickness of the adsorbed film, etc.

Determination of Surface Coverage θ

The surface coverage with adsorbed monomer units can be calculated[1,2,6,12,29] from data on the displacement of the zero-charge or isoelectric point as a consequence of adsorption. The basis of the first method, originally developed for the adsorption of organic molecules on a mercury electrode, is that, in the absence of specific adsorption of ions, the shift in the zero-charge point is proportional to the number of adsorbed molecules per unit area[7]:

$$\Delta_{zcp} = \text{const} \cdot n_a. \tag{8}$$

The shift is attributed in this case to displacement of water dipoles from the surface layer by adsorbed molecules of a surface-active substance. Transfer of these ideas to the adsorption of macromolecular compounds encounters several difficulties, which have been analysed in detail by Lyklema et al.[1,2,12] for the example of silver iodide and polyvinyl alcohol solution. The first difficulty is that the thermodynamics of surface phenomena, used to analyse the electrical double layer in the presence of organic compounds, is applicable only to reversible adsorption processes. Although the adsorption of polymers is irreversible with respect to change in their concentration in solution, it may be reversible with respect to change in concentration of potential-determining ions. Furthermore, the requirement of reversibility concerns only a small proportion of the total quantity of monomer per units adsorbed (those in direct contact with the surface), which is apparent on the measurement of surface charge. The second difficulty is the difference in surface area accessible to macromolecules and to potential-determining ions. Therefore an "average" charge σ_{av} (Eqn.1) is normally used in the calculation of surface coverage.

According to Frumkin[70] the charge $\sigma(\theta)$ on a surface partly covered with surface-active molecules can be written as a linear combination of the charge σ_0 on an uncovered surface and the charge $\sigma(\theta=1)$ on the surface completely (100%) covered with adsorbate:

$$\sigma(\theta) = (1-\theta)\sigma_0 + \theta\sigma(\theta=1). \tag{9}$$

This relation has been used[1,2,12] to calculate the surface coverage of silver iodide with adsorbed polyvinyl alcohol $[CH_2.CH(OH)]_n$ on the basis that the adsorption of monomer units directly attached to the surface is a reversible function of pAg. Here the Stern layer can be regarded as comprising $\frac{1}{2}\theta$ $CH_2 + \frac{1}{2}\theta$ $CH(OH) + 1 - \theta$ vacancies. The symbols $\sigma(\theta)$ and σ_0 denote the measured surface charge densities in the presence and in the absence of adsorbed polyvinyl alcohol, while $\sigma(\theta=1)$ is found indirectly by regarding the Stern layer at maximum surface coverage as a hypothetical layer 50% covered with CH_3 (as in the case of butanol) and 50% with CH(OH) groups (as for ethylene glycol). Thus at a given ψ_0-potential

$$\sigma_{pva} = (1-\theta)\sigma_0 + \frac{1}{2}\theta[\sigma(\theta=1)_{BuOH} + \sigma(\theta=1)_{egl}], \tag{10}$$

or for the shift in the zero-charge point

$$\Delta_{zcp,\,pva} = \frac{1}{2}\theta[\Delta_{zcp.}(\theta=1)_{BuOH} + \Delta_{zcp.}(\theta=1)_{egl}]. \tag{11}$$

The surface coverage in the first (dense) layer of units is clearly $\theta = n_a(\theta)/n_a(\theta=1)$, or from Eqn.(8) [29]

$$\theta = \frac{\Delta_{zcp.}(\theta)_{pva}}{\Delta_{zcp.}(\theta=1)_{pva}} = \frac{2\Delta_{zcp.}(\theta)_{pva}}{\Delta_{zcp}(\theta=1)_{BuOH} + \Delta_{zcp.}(\theta=1)_{egl}}, \tag{12}$$

where n_a is the number of adsorbed units per unit surface area. The calculation was based[1,2,6,12] on published values of the shift in the zero-charge point of silver iodide on the adsorption of butanol and ethylene glycol[7,30] and measured values of $\Delta_{zcp}(\theta)_{pva}$. The maximum surface coverage was found to be $\theta = 0.85$: i.e. even with complete surface coverage of silver iodide with polyvinyl alcohol 15% of the Stern layer is "vacant" for the polymer.

Surface coverage can be calculated also[1,2,12] from electrophoretic data—from the change in the isoelectric point of particles in the presence of adsorbed polymer—which has the advantage that the isoelectric point can be measured more accurately than the zero-charge point. Moreover, the former measurements can be made on particles of a sol, whose surface, in contrast to the suspensions on which surface charge density is measured, are completely accessible to adsorbed macromolecules.

The fact that the initial portions of polyvinyl alcohol adsorbed on silver iodide produce the largest shifts in the isoelectric point, after which the latter reach saturation, has enabled[1,2] surface coverage to be calculated from the relation

$$\theta = \frac{\Delta_{iep.}(\theta)}{\Delta_{iep}(\theta=1)}\theta_{max}. \tag{13}$$

where $\theta_{max} = 0.85$. Fig.10 shows that, with increase in adsorption, surface coverage of silver iodide by monomer units increases rapidly to ~0.7 mg m^{-2}, which indicates that the greater part of the polymer has been adsorbed as a flat layer having many contacts with the surface. Further adsorption is accompanied by a slow increase in coverage, the excess of polymer accumulating as spikes and loops.

Determination of surface coverage by the two methods gives closely similar results. It is significant that the coverage is determined mainly by the quantity of polyvinyl alcohol adsorbed, and is little dependent on the molecular mass or the content of acetate groups.

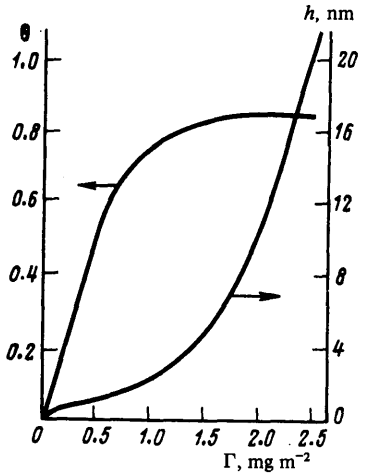


Figure 10. Effects[2,112] of quantity of polyvinyl alcohol adsorbed on surface coverage θ of silver iodide particles and on thickness *h* of adsorbed layer.

Determination of Proportion of Monomer Units in Direct Contact with Surface ν

From data on surface coverage for various quantities of polymer adsorbed Γ (in mg m^{-2}) we can calculate also an important parameter of the adsorbed layer—the proportion of monomer units in a macromolecule that are in direct contact with the surface[12]:

$$\nu = [M_{mu}/N_A a_0]\theta/\Gamma, \qquad (14)$$

where N_A is Avogadro's number, M_{mu} the molecular mass of a monomer unit, and a_0 (nm^2) the area occupied by one unit. This area can be calculated from the density of the dry polymer and its molecular mass as the projected area of the effective hydrodynamic sphere. Monomer units of water-soluble polymers can be assumed[23,29,61] to be adsorbed with the whole firmly bound hydration sphere, which e.g. for polyvinyl alcohol and polyethylene oxide comprises two water molecules per monomer unit[62,63]. Therefore the calculation of a_0 must take account also of coordinated water. This gives values of 0.30 and 0.28 nm^2 respectively for $[CH_2.CH_2.O].2H_2O$ and $[CH_2.CH(OH)].2H_2O$. Fig.11 illustrates the ν(Γ) dependence calculated from Eqn.(14) for the adsorption of polyvinyl alcohol on silver iodide. Even at low surface coverage with the polymer ν ≠ 0.4–0.5, while the proportion of units attached to the surface diminishes with increase in polymer adsorption, in good agreement with other measurements[5,71,72].

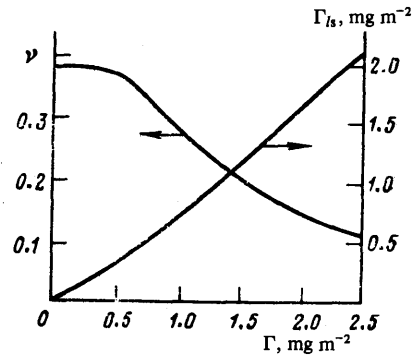


Figure 11. Dependence[12] of proportion ν of monomer units directly in contact with surface and of quantity Γ_{ls} of polymer present as spikes and loops on quantity of polyvinyl alcohol adsorbed on silver iodide particles.

The Reviewers evaluated ν from data on the number of contacts of an adsorbed macromolecular chain with the surface calculated from values of $\Delta\sigma_i$ for the surface of antimony sulphide particles during the adsorption of polyethylene oxide[19]. The total potential difference between the phases consists of ionic and dipolar components[13] (Section I), and the proposed method is based on the view that, in solutions of moderate ionic strength, the major part of the potential difference occurs in the dense region of the double layer, whose thickness is comparable with the length of a monomer unit in polyethylene oxide(0.4–0.5 nm). With an insignificant change in capacitance of the double layer in the presence of the polymer the condition of constant surface potential can then be replaced by constancy of the surface charge: $\sigma = \sigma_i + \sigma_d = \text{const}$, where σ_i is the ionic component of the surface charge, and σ_d the total charge of the ends of adsorbed dipoles oriented along the normal to the surface. By equating the observed value of $\Delta\sigma_i$ to σ_d we can calculate the number *n* of ends of dipoles oriented in the adsorbed polymer layer from the relation $\Delta\sigma_i = \sigma_d = Dn/l$, where *D* (in D) is the dipolar moment of a monomer unit and *l* the length of a dipole.

The results[19] indicate that (i) for a given quantity of polyethylene oxide adsorbed the number of contacts between polymer and surface is independent of molecular mass, (ii) with increase in surface coverage the proportion per adsorbed molecule of units in contact with the surface diminishes, and (iii) even with small amounts adsorbed the proportion of units directly attached to the surface does not exceed one-third of the total number of adsorbed units, in good agreement with published values for other polymer–solid systems[5,71–74].

Calculation of Quantity of Polymer in Loops and Spikes Γ_{ls}

From data on the area a_0 occupied by a monomer unit and the surface coverage θ it is easy to calculate the quantity of polymer Γ_1 in direct contact with the surface, i.e. in the first (dense) part of the adsorbed film. Subtraction from the total quantity adsorbed Γ will then give the quantity of polymer Γ_{ls} present on the surface as loops and spikes. Fig.11 illustrates the variation in Γ_{ls} with increase in the adsorption of polyvinyl alcohol on silver iodide particles[12].

Determination of Thickness of Adsorbed Film *h*

The adsorption of macromolecular compounds usually lowers the electrokinetic potential of particles (above). If the surface charge of the latter is not significantly changed[19, 23,50], it can reasonably be assumed that the observed decrease in potential is due primarily to displacement of the slippage plane into the liquid phase as a result of surface formation of adsorbed films of increasing thickness. In such case, even if adsorption leads to a change in surface charge density, it is usually observed at low surface coverage, and can be allowed for in the calculation of electrokinetic potential.

Film thickness can be calculated from $\zeta-\Gamma$ relations plotted from a comparison of adsorption and electrokinetic measurements on the same system. The method involves calculating the shift in the slippage plane, which is identified with the effective thickness of the polymer sheath relative to the boundary of the Stern layer. It is assumed that the adsorbed polymer does not affect the distribution of potential in the double layer and that the polymer sheath is hydrodynamically impermeable. From the equilibrium distribution of potential in the vicinity of the particles we can then calculate for each measured ζ-potential the coordinates of the slippage plane, by means of the well known theoretical formula of the diffuse double layer[13]

$$\tanh\left(\frac{ze\zeta}{4kT}\right) = \tanh\left(\frac{ze\psi_\delta}{4kT}\right) e^{-\varkappa x}, \quad h = x + \delta, \qquad (15)$$

in which $\varkappa^{-1}$ is the Debye shielding radius, z the valency of the gegenions, e the elementary charge, δ the thickness of the Stern layer, and x the distance from the slippage plane to the boundary of this layer, the ψ_δ-potential usually being equated to the ζ-potential in the absence of polymer. This method has been used to calculate film thickness h for the adsorption of polyethylene oxide and polyvinyl alcohol on particles of silver iodide and antimony sulphide[23,24,50,61,75] as well as on latices[76].

The results show that the adsorbed layers increase in thickness to several tens of nanometres with increase in polymer adsorption (Fig.12). It is significant that at a given adsorption the thickness varies little with molecular mass, and for polyvinyl alcohol with the content of acetate groups[23,24,50,61]. This implies that the mean length of adsorbed loops and spikes is also little affected by molecular mass. The values found for the film thickness agree to within 20–50% with those obtained by other methods—for polyvinyl alcohol on silver iodide viscosimetrically[6,29], for polyethylene oxide on the same surface by electron microscopy[77], and for polyvinyl alcohol on latex particles by measurement of precipitate volume, ultracentrifugation, and diffusion[76].

The present method has been criticised[2] on the grounds firstly that difficulties are involved in calculating electrokinetic potentials from electrophoretic mobility data owing to polarisation of the double layer, and secondly that the true potential at the boundary of the Stern layer is usually unknown and its replacement by ζ_0 is an approximation. It must be borne in mind also[50,51,76] that formula (15) gives the potential distribution in a planar double layer, and its

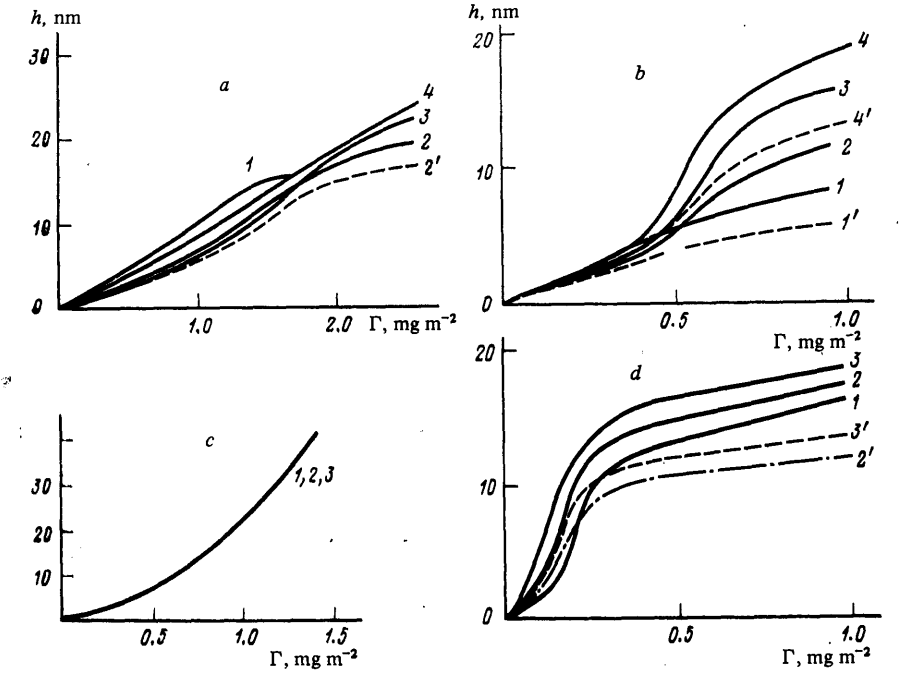


Figure 12. Variation, calculated from electrophoretic measurements[24], of thickness of polymer sheath on sol particles with quantity of polymer adsorbed. Lettering of diagrams and numbering of curves as in Figs.3 and 6 [sic].

application is valid only provided that $\kappa a \gg 1$. Furthermore, the condition of hydrodynamic impermeability of the adsorbed polymer layer may break down in solutions of high electrolyte concentrations[51].

One of us[51] used the adsorption of polyethylene oxide on fine particles ($a \approx 11$ nm) of antimony sulphide as example to make a detailed analysis of the influence of various complicating factors—polarisation of the double layer, curvature of the surface, presence of electrolytes—on the calculation of film thickness from electrophoretic data. With κ, a, and Rel having the respective values 1, 3, and 2 (the parameter $\mathrm{Rel} = e^{\frac{1}{2}\psi\delta - 1}/\kappa a$ represents the contribution by polarisation of the double layer to surface electrical phenomena; this polarisation can be neglected when $\mathrm{Rel} \ll 1$ [60,78]), i.e. when polarisation of the double layer must be taken into account, film thicknesses found from electrokinetic potentials calculated with and without allowance for such polarisation ζ_W§ and ζ_S differ by at most 10%. Such a small difference in thickness with a substantial difference in electrokinetic potentials ($\zeta_W \cong 2\zeta_S$) is due firstly to the occurrence of the distance of the slippage plane from the surface in the exponent in Eqn.(15), so that the thickness is insensitive to the ζ-potential, and secondly to the dependence of h not on absolute values of ζ but on the ratio of their hyperbolic tangents. A more substantial error in the thickness is due to disregard of surface curvature: values of h calculated from formulae for a spherical double layer are usually smaller than those calculated for a planar surface[50]. From results obtained[79] with the condition $\kappa h < 1$ a first correction for surface curvature will yield for spherical particles the formula[51]

$$\kappa h = \left[\left\{\tanh\left(\frac{ze\zeta_0}{4kT}\right)\Big/\tanh\left(\frac{ze\zeta}{4kT}\right)\right\} - 1\right]\left[1 - \left\{1/\kappa a \cosh^2\left(\frac{ze\zeta_0}{4kT}\right)\frac{\mathrm{th}\,(ze\zeta_0/4kT)}{\mathrm{th}\,(ze\zeta/4kT)}\right\}\right]. \quad (16)$$

This shows that the error when h is determined without any correction for curvature increases as ζ and κa decrease: whereas with $\kappa a = 5$ and $\zeta_0 = 100$ mV the error is only 2–3%, when $\kappa a \approx 1$ the formula from which (16) was obtained itself gives an error already exceeding 10%.[79] In general, when both surface curvature and concentration polarisation of the double layer are taken into account, the use of formula (15) with ζ-potentials determined by Smolukhovskii's method with $\kappa a \leq 1$ may produce significant distortion of the results. Thus comparison of h calculated by means of Eqn.(15) with thicknesses determined from results[81] for ζ_0 values of 50, 100, and 150 mV gives differences of 49%, 73%, and 65% respectively[51].

It was shown[51] also that the increase in effective particle radius due to polymer adsorption must also be taken into account in the calculation of thickness, i.e. that it is more correct to use $\kappa(a+h)$ instead of κa, but then the parameter h itself must be determined. This requires a set of equations to be solved, one of which defines the dependence of the equilibrium potential on the distance from the particle surface with a known potential ζ_0, while the second is obtained from the dependence of the observed electrophoretic mobility on the ζ-potential and the corresponding quantity $\kappa(a+h)$. Analytical solution of such a problem is quite laborious, even when a computer is used, so that one of us has suggested a graphical method (see Ref.51 for details). Thicknesses obtained in this way will be the most accurate, since polarisation of the double layer, curvature of the surface, and variation in effective particle radius during coating with thickening adsorbed polymer films have all been taken into account.

§The ζ_W potential is calculated in this case from Wiersema's tables[80].

It was shown also[51] that thicknesses of polyethylene oxide on antimony sulphide particles calculated from electrokinetic potentials in relatively concentrated (>0.01 M) electrolyte solutions are improbably small (≤3 nm). This may be due to enhancement of permeability of the adsorption sheath with increase in ionic strength of the solution. In such case the slippage boundary, from which the layer thickness h is assessed, will pass into this layer and move nearer the surface of the dispersed phase. Under these conditions the determination of thickness from electrophoretic data on the basis of the above simple ideas is incorrect. New possibilities for calculating h in the case of permeable adsorbed layers are revealed by a theory developed recently[64].

In view of the above limitations and difficulties involved in calculating thickness from the fall in the electrokinetic potential, Lyklema[2] suggested calculating h on silver iodide particles from the slope of the experimental variation in ζ as a function of pAg at or near the isoelectric point. The basis of the proposed method was the decrease in slope with increase in h. For a planar double layer in a uni-univalent electrolyte the equation

$$\left(\frac{d\zeta}{dpAg}\right)_{\sigma\to 0} = 58.16\,\frac{\mathrm{sech}^2(e\psi_\delta/4kT)}{\mathrm{sech}^2\,(e\zeta/4kT)}\,\frac{C}{C_d}\exp(-\kappa h), \quad (17)$$

was derived, and use of the Debye–Hückel approximation gave

$$\left(\frac{d\zeta}{dpAg}\right)_{\sigma\to 0} = 58.16\,\frac{C\exp(-\kappa h)}{C_d(a+h)} \quad (18)$$

for a spherical double layer[2,12]. In these equations C is the total capacitance of the double layer, which can be found from potentiometric data, while the capacitance C_d of the diffuse ionic layer can be obtained from the theoretical relation $C^{-1} = C_m^{-1} + C_d^{-1}$ provided that the surface potential and the electrolyte concentration are low (C_m is the capacitance of the molecular capacitor, which is usually 20 $\mu F/cm^{-2}$). The value of ψ_δ in Eqn.(17) is calculated from data on surface charge density determined by titration. Thus the only unknown in Eqns.(17) and (18) is h. The variation in the thickness of the polymer sheath calculated in this way for the adsorption of polyvinyl alcohol or particles of silver iodide is shown in Fig.10. The results are somewhat smaller than viscosimetric values for the same system and thicknesses of this polymer on latex particles measured by hydrodynamic methods[6,26,76]. Nevertheless, the course of the $h-\Gamma$ dependence and the absolute thicknesses are closely similar to those found from the fall in the electrokinetic potential (above).

Our discovery of a decrease in the relative conductivity of dispersions having a polymer sheath for values below those predicted theoretically suggests a new method for estimating film thickness. Its basis is that appearance of a "hypertheoretical" slope in the plots of $\bar{K}/K$ against p during adsorption is associated with an increase in relative particle volume due to formation of an adsorbed polymer layer within which water is immobilised. The difference Δp corresponding to points of intersection of a straight line parallel to the abscissae axis with the $\bar{K}K^{-1}-p$ straight lines for suspensions with and without added macromolecular compounds gives the increase in relative volume due to polymer adsorption. From this difference and the corresponding volumes it is easy to calculate h. For the adsorption of polyvinyl alcohol on palygorskite particles, for example, the resulting thickness (~15 nm) is extremely plausible.

Knowing the film thickness for various adsorbed quantities and parameters of macromolecular coils in solution found by viscosimetric or optical (light-scattering) methods, we can define a probable model for the adsorption of non-ionic polymers on colloidal particles. The Reviewers' calculations for the adsorption of polyvinyl alcohol and polyethylene oxide on silver iodide and antimony sulphide particles[50,82] enabled them to eliminate for these systems a model of monomer units arranged flat on the surface in the form of similar (equal-sized) loops with a regular alternation of units attached to the surface along the macromolecular chain, and also as undeformed random coils. Calculated values of h were appreciably less than double the radius of inertia of a polymer coil in solution $2\langle s^2\rangle^{\frac{1}{2}}$ (thus for polyethylene oxide of molecular mass 2.3×10^5 on antimony sulphide with $\Gamma = 1.0$ mg m^{-2} we have $h = 20$ nm, whereas $2\langle s^2\rangle^{\frac{1}{2}} \approx 50$ nm [82]), the difference between $2\langle s^2\rangle^{\frac{1}{2}}$ and h increasing rapidly with increase in molecular mass[50,83]. These facts indicate appreciable deformation of the macromolecular coils of these polymers when adsorbed on the above inorganic surfaces.

The experimental results can be explained satisfactorily by the Bulas–Hoeve–Hesselink model of an adsorbed film[60–69,83], according to which the polymer sheath on the surface consists of a denser first layer and a layer of dissimilar loops and spikes pointing towards the liquid, with an exponential size distribution. At the boundary of the first layer the density of segments changes abruptly, while beyond this layer the variation $\rho(x)$ along the normal to the surface is described for homopolymers by the exponential relation[68]

$$\rho(x) = 12\frac{x}{il_{st}^2}\exp\left(-6x^2/il_{st}^2\right), \qquad (19)$$

in which l_{st} is the length of a statistical chain unit (segment) and i the number of segments in a loop. It can be shown for such a model that the mean number of segments in a loop $\bar{i}$ and the length l_{st} are interrelated[6,29]:

$$\bar{i} = 2b\sqrt{6}/l_{st}\,p_H, \qquad (20)$$

where b is a numerical constant approximating to 0.7 [6,29] and the parameter p_H is a function of the proportion ν of units attached to the surface (it is calculated as the ratio of the number n_1 of units in the first layer to their total number n per unit surface; n_1 has been calculated from the area occupied by a unit together with the surface coverage θ found by the above method) and the dimensionless constant $K_H < 1$ determined by the flexibility of the polymer chain. This constant is evaluated by calculating from the relation[6,29]

$$h - \delta' = \frac{n-n_1}{K_H\rho_0}\ln\left(\frac{K_H\rho_0}{\rho_{eff}}\right) \qquad (21)$$

(which holds for $\Gamma \geq 0.5$ mg m^{-2}) the theoretical dependence of layer thickness h on quantity of polymer adsorbed that best coincides with the experimental curve. Here δ' is the thickness of units in the first layer, $\rho_0\delta' = n_1$, and the effective density of the adsorbed film ρ_{eff} is calculated from the theory of polymer solutions as the density of a statistical coil of radius equal to the thickness of the polymer sheath. Thus the same variation of density of segments with distance is assumed in the adsorbed film (from the surface) and in the statistical coil (from its centre of gravity): i.e. $\rho_c(i) = \rho_{eff}$ and $\bar{i} = h$. This, of course, is only an approximation, but is fairly accurate, since the thickness found from formula (21) is not very sensitive to the effective density[6,29]. For example, with $K_H = 0.8$ and $10^4\rho_0 = 70$ Å^{-3} the value of h decreases by only 17% for an increase in ρ_{eff} of 50%.[29]

The Reviewers' experimental results[23,25] on the adsorption of polyvinyl alcohol on silver iodide and on antimony sulphide corresponded most closely to the values 0.3 and 0.25 respectively for K_H; for polyethylene oxide on silver iodide K_H varied from 0.07 to 0.1 depending on the molecular mass of the specimen. From values of $\bar{i}$ calculated in this way it is easy to find the number of groups adsorbed by unit surface as $N_1 = n_1/\bar{i}$, where n_1 is the number of units attached as loops to the surface, calculated as the difference between n and n_1.

Table 3. Parameters of macromolecular chains of polyvinyl alcohol and polyethylene oxide in surface layer of silver iodide particles[23,50].

Polymer	10^{-4} M	Γ_1, mg m^{-2}	$\bar{i}$ with Γ (mg m^{-2})			$10^{-16}N_1$, m^{-2}
			0,4	0,7	1,0	
pva-12	2.2	0.17	3.8	6.6	13	11.6
peo-1	23	0.15	21	50	78	6.6
peo-2	130	0.15	23	55	87	5.9
peo-3	260	0.15	32	76	120	4.3

Thus combined adsorption, electrokinetic, and viscosimetric measurements open up a path to determination of the most important parameters of adsorbed polymer films—the number and length of loops N_1 and $\bar{i}$ adsorbed by unit area—which are required for theoretical calculation of the energy of repulsion V_R of colloidal particles covered with a polymer sheath. Table 3 lists several parameters of macromolecular chains of polyethylene oxide and polyvinyl alcohol on the surface of silver iodide and antimony sulphide particles found by the above method. The Reviewers have used them to calculate the polymer component of the energy of repulsion of the particles and for a theoretical interpretation of the stabilisation of the sols by additions of these polymers[57,58,84].

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The Introduction of Tritium into Biologically Active Compounds with the Aid of Exchange Methods

L.A.Neiman

Different versions of the homogeneous and heterogeneous catalytic isotope exchange as well as catalytic substitution of a halogen by tritium are examined from the standpoint of their use for the introduction of a tritium label into compounds of biological interest (aminoacids, peptides, proteins, nucleotides, carbohydrates, steroids, medicinal agents, etc.). The bibliography includes 214 references.

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I. INTRODUCTION

Biology and related disciplines—biochemistry, molecular biology, and bio-organic chemistry—are fields of study where the use of isotope exchange has proved most fruitful. The present development of a whole series of branches of these sciences could not be imagined without the utilisation of radioactive isotopes and some branches (for example, the study of metabolism or biogenesis) have been placed on a genuine scientific basis solely as a result of the application of the isotope method. Isotope exchange has now come to be widely used in biochemistry and bio-organic chemistry as a method for the qualitative and quantitative analysis of substances. The reason for this is that isotope exchange is more sensitive by 4–6 orders of magnitude than spectroscopic methods and moreover in most instances does not require careful purification of the substances to be determined. It is frequently actually unnecessary to isolate them or to comminute the sample in which they are contained. The high sensitivity of the isotope method is particularly important for biological disciplines, because it permits a reliable determination of the substances at concentrations close to those at which their biological activity is shown.

Since the sensitivity of the method is unambiguously related to the specific radioactivity a of the labelled compound, there has arisen in recent years a clear tendency to use tritium-containing organic compounds instead of their analogues labelled with ^{14}C. Indeed, when a single T atom is introduced into a molecule, a ~30 c mmol^{-1} should be attained theoretically, while the introduction of a single ^{14}C atom yields only 64 μc mmol^{-1}. Since the molecules of organic compounds contain in many instances tens of hydrogen atoms, it is in principle possible to obtain tritiated compounds with a amounting to several hundreds and more of c mmol^{-1}. However, in practice preparations with $a > 50$–100 c mmol^{-1} are rarely used, because under the conditions of high values of a autoradiolysis is accelerated. Other advantages of tritium are the possibility of introducing it by exchange methods (i.e. into a "finished" molecule) and a much lower cost of tritium-containing compounds compared with those labelled with ^{14}C. As regards other radioactive isotopes employed (^{32}P, ^{33}P, ^{35}S, ^{125}I, etc.), the region of their applicability is naturally much narrower.

Thus tritium is nowadays the most important and most common radioactive isotope used in biology and related disciplines and the problem of methods of synthesising tritium-labelled biologically active substances (BAS)† has become extremely urgent. These methods include chemical synthesis, biosynthesis, synthesis with the aid of hot atoms, and exchange methods (catalytic isotope exchange, the Wilzbach method and its modifications, etc.), the exchange methods having a number of advantages particularly in the preparation of labelled BAS of complex structure—these are primarily single-stage synthesis ("rapidity" of synthesis), universality, comparative simplicity, and the possibility of obtaining high values of a.

This review is devoted to exchange methods for the preparation of tritium-containing BAS; the exchange of labile hydrogen atoms and homogeneous and heterogeneous catalysis of the hydrogen–tritium exchange are considered in detail. Furthermore, the review includes the method of catalytic dehalogenation, which is strictly speaking one of the synthetic methods. This is because of, firstly, its similarity (both from the standpoint of the mechanism and from the standpoint of the purely preparative aspect) to the heterogeneous catalysis of isotope exchange and, secondly, because of the extremely great importance which the method has assumed (particularly in recent years) for the preparation of virtually all classes of labelled BAS, in the first place peptides, proteins, and nucleotides. The Wilzbach method and its modifications are not considered in this review. Attention has been concentrated on studies published in the last ten years; a compilation of earlier literature can be found in Evans's monograph published in Russian translation[1] in 1970. Studies on deuterium are quoted only in those cases where it is of interest to compare them with the corresponding results for tritium or when such results for tritium are not available at all but the latter could be obtained (judging from the studies using deuterium).

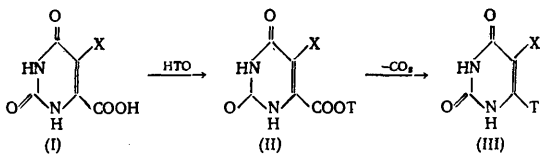
II. EXCHANGE OF LABILE HYDROGEN ATOMS

On dissolution, compounds containing the >NH, –OH, and –SH groups in protic tritium-containing solvents (HTO, MeOT, EtOT, AcOT, etc.) are known to exchange rapidly the H

† In the present review biologically active substances (BAS) are understood to be both products of natural origin (proteins, peptides, aminoacids, carbohydrates, nucleotides, steroids, etc.) and synthetic preparations (medicinal agents, pesticides, carcinogens, etc.).

atoms of these groups (labile hydrogen atoms) for T even under the usual conditions. If the solute is capable of undergoing tautomeric transformations (for example keto–enol or imine–enamine tautomerism), the H atoms linked to the C atoms can also exchange with the tritium-containing solvent under conditions (frequently fairly mild) under which a tautomeric equilibrium is established (i.e. the stable H atoms become labile).

The introduction of tritium in a labile position takes place readily and reversibly, so that the reaction is as a rule of no preparative value, since the labelled BAS obtained by this method lose tritium completely on dissolution in the usual solvents or on being employed in biological studies. However, in certain cases tritium can be fairly simply transferred from a labile to a stable position. An excellent example is provided by the synthesis of 5-fluorouracil-6-*t* [2–5] and 5-bromouracil-6-*t* [6] from the corresponding orotic acids (I), which readily exchange their carboxyl hydrogen on heating with HTO or (the preferred method) [4,5] with a solution of T_2O in dioxan or dimethylformamide (DMF) (100 °C, 1 h). Such solutions are obtained as a result of passing T_2 through a suspension of PtO_2 in dioxan or DMF. Labelled orotic acids (II) are then decarboxylated at 250–300 °C with formation of the corresponding tritiated nucleic bases (III) having $\alpha \cong 1$–2 c mmol^{-1}. It has been shown[7] that thymine-6-*t* can be obtained similarly:



(I) (II) (III)

X = Br, F, or Me.

The same principle constitutes the basis of a method for the specific introduction of D or T into the α-position in α-aminoacids (alanine, phenylalanine, glutamic acid, and aspartic acid)[8]. The method involves the isotope exchange of the carboxyl hydrogen in the corresponding *N*-acylaminomalonic acid (IV) with D_2O or HTO and subsequent hydrolysis and decarboxylation. All three stages can be carried out in a single experiment:

$$\underset{(IV)}{RCONHCR'(COOH)_2} \xrightarrow{HTO} RCONHCR'(COOT)_2 \xrightarrow[HTO]{\Delta} RCOOH + H_2NCT(R')COOH.$$

III. HOMOGENEOUS CATALYSIS OF HYDROGEN ISOTOPE EXCHANGE

Both base and acid catalysis as well as catalysis in the presence of soluble transition metal salts have been used to introduce tritium into BAS.

1. Base Catalysis

In base catalysis the isotope exchange process is initiated as a result of attack by a B^- anion, which abstracts a proton from the compound involved in exchange with formation of a carbanion, which then combines with T^+. If the intermediate carbanion is an ambident species [for example, (V)], i.e. can be protonated at two (or more) centres, the conditions for isotope exchange are the same as the conditions for tautomeric transformations and the latter can be frequently identified from the occurrence of isotope exchange:

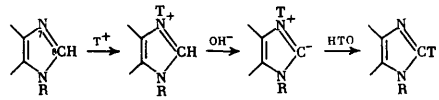
$$R_2CH{-}C(R')=X \xrightarrow{B^-} [R_2C\cdots C(R')\cdots X]^- \xrightarrow{T^+} R_2CT{-}C(R')=X +$$
(V)

$$+ R_2C=C(R'){-}XT \quad ;$$

X=O, N–, C< .

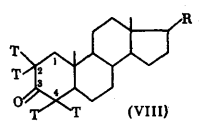
In certain cases the deprotonation proceeds very readily. Thus purine bases, nucleosides, and nucleotides exchange hydrogen, albeit slowly, at $C_{(8)}$ even at pH 8 and room temperature[9,10]. In the preparative synthesis of labelled purines it is necessary to heat the latter with HTO at 85–100 °C; the reaction time varies from 20 min (for DNA and nucleoside triphosphates, which undergo hydrolysis under these conditions) to several hours[11–13]. The rate of exchange is determined by both electronic and steric factors. The presence of a ribofuranosyl residue facilitates the exchange: at 85 °C adenosine exchanges at $C_{(8)}$ twice as fast as adenine which, however, exchanges hydrogen at $C_{(2)}$ 2000 times faster than at $C_{(8)}$.[14]

The conformation of the macromolecule and the microstructure of the helix which determine the accessibility of a particular section of the nucleic acid molecule to water, exert a significant influence[15–18]: the exchange of H at $C_{(8)}$ with HTO in the purine residues of a natural double helix DNA is almost three times slower than for a mixture of the corresponding polynucleotides; the double helix RNA exchanges even more slowly (by a factor of 30–40). Studies of the kinetics of the exchange at different pH have shown[19–22] that in reality the $N_{(7)}$-protonated form (VI) and not the purine molecule itself is deprotonated. The former is formed very rapidly, while its conversion into the ylid (VII) is the rate-limiting stage in the entire process:



(VI) (VII)

Methylene groups activated by neighbouring electron-accepting groups (>CO, –COOR, –CN, etc.) exchange with HTO at alkaline pH, usually with heating. For ketones, for example camphor[23], the exchange proceeds under conditions identical with those for enolisation, and the isotope exchange mechanism is in this case identical with the mechanism of tautomeric keto–enol transformations. In order to introduce T into the α-position relative to the oxo-group in testosterone, progesterone, and other 3-oxosteroids, a convenient preparative method has been proposed[24,25]. It consists in passing a solution of the test substance in an organic solvent through a column filled with basic alumina subjected to a preliminary treatment with HTO. Tritium has been introduced into the 2- and 4-positions of 3-oxo-5α-cholestan-26-yl acetate (VIII) by a similar procedure—isotope exchange with iso-PrOT in the presence of aqueous NaOH:[26]



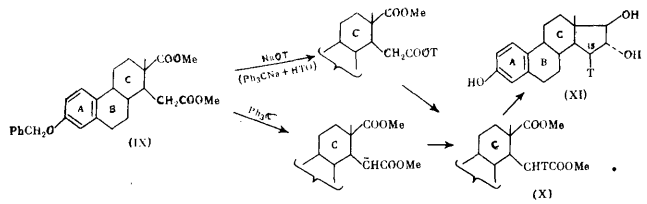
(VIII)

The tritium atoms introduced by these procedures into the steroid molecule are entirely stable in acid and neutral media, but at pH > 10 they exchange for H to the extent of 80–95% even at the usual temperature over a period of 24 h.

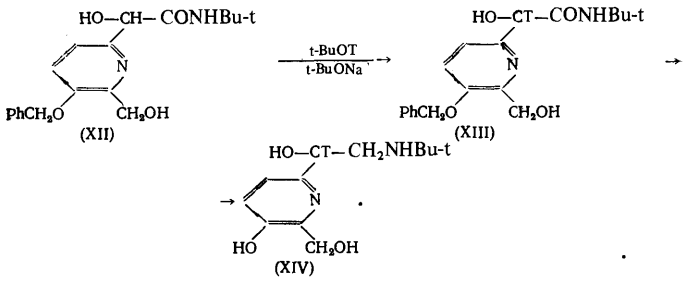
Isotope exchange involving the hydrogen in a methylene group activated by neighbouring carbonyl groups proceeds readily in an alkaline medium also in aminosugars (pH 11–11.5; 20 °C; 48 h), as shown for example, for 2-acetamido-2-deoxy-D-glucose[27], where deuterium can be introduced in the 2-position by this procedure with a high yield. Since alkaline epimerisation also takes place under these conditions 2-acetamido-2-deoxy-D-mannose-2-C-*d* is formed as a side product.

Steroid lactones—cardiac glycosides of the digitoxin series and their aglycones—exchange with HTO in DMF in the presence of Et_3N (30–80 °C, 2–8 h), more than 95% of tritium being incorporated in the lactone ring. Tritium-labelled digitoxin, digitoxigenin, digoxin, gitoxigenin, and uabain with $a \cong 0.4$–0.7 c mmol^{-1} have been obtained by this method[28].

Homogeneous base catalysis has also been used in the synthesis of triol-15-*t* (XI).[29] The 3-benzilate of the dimethyl ester of marianoleic acid (IX) is tritiated in the α-position relative to the methoxycarbonyl group on successive treatment with triphenylmethylsodium and HTO and the resulting labelled ester (X) was converted by acyloin condensation and subsequent reduction into 15-tritioestriol (XI); this compound contains a tritium atom in a position within the molecule from which it cannot be removed by the water present in living organisms:



The isotope exchange between the *N*-t-butylamide of 2-(5-benzyloxy-6-hydroxymethyl-2-pyridyl)-2-hydroxyacetic acid (XII) and t-BuOT in the presence of t-BuONa takes place readily (20 °C; 16 h). The resulting amide-α-*t* (XIII) serves as the starting material for the synthesis (reduction with B_2H_6 and subsequent catalytic debenzylation) of the labelled medicinal preparation pirbuterol (XIV):[30]

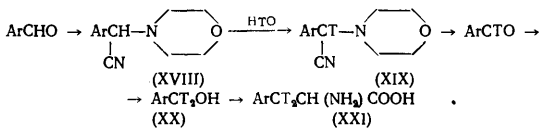


The hydrogen atoms of the α-methylene group are mobile not only in lactones, esters, and acid amides (as can be seen from the examples quoted above) but also in the carboxylic acids themselves. The sodium or potassium salts of aliphatic acids (ranging from butyric to stearic) are converted in high yields into salts of α-labelled acids (XVI) and (XVII) on heating with NaOH and D_2O or HTO under severe conditions (autoclave; 200 °C; 1–3 days) with intermediate formation of the corresponding carbanions (XV):[31]

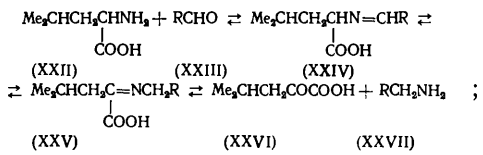
$$RCH_2COOK \rightarrow \underset{(XV)}{R\bar{C}HCOOK} \rightarrow \underset{(XVI)}{RCHTCOOK} \rightarrow \underset{(XVII)}{RCT_2COOK} .$$

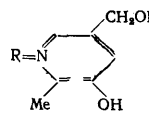
The α-hydrogen atoms in lactic[32], chrysanthemic[33], and abscisic[34] acids exchange for *D* or *T* under similar conditions and in the last case tritium also enters the 4-position and the methyl group linked to $C_{(5)}$; the preparation obtained has a high activity $a \cong 6.5$ c mmol^{-1}.

The isotope exchange involving aminoacids is unsatisfactory under these conditions. Labelled aminoacids are therefore prepared by other, more complex methods; some of these also involve isotope exchange catalysed by bases. For example, under the influence of morpholine and an aqueous NaCN solution, aromatic aldehydes are readily converted into morpholinoacetonitriles (XVIII), which exchange hydrogen in the α-position relative to the cyano-group on heating with D_2O or HTO (DMF or sulpholan; 100 °C; ~5 h).[35] Hydrolysis of the labelled nitriles (XIX) leads to aldehydes containing tritium in the formyl group; on disproportionation of these aldehydes via the Cannizzaro reaction, the corresponding benzyl-α,α-t_2 alcohols (XX) are formed and are then converted by familiar synthetic methods into aromatic aminoacids (phenylalanine, tyrosine, and dihydroxyphenylalanine) labelled with tritium in the β-position [compound (XXI)]:



A novel possibility for hydrogen isotope exchange in aminoacids under the conditions of base catalysis was demonstrated with deuterium for leucine (XXII),[36] which is converted into leucine-α,β,β-d_3 on boiling in D_2O in the presence of pyridoxal (XXIII) and potassium alum. Under these conditions, an equilibrium is established between leucine and pyridoxal, on the one hand, and the ketoacid (XXVI) and pyridoxamine (XXVII), on the other, with intermediate formation of the corresponding Schiff bases (XXIV) and (XXV). The tautomerism of these bases (XXIV) ⇌ (XXV) in D_2O is in fact responsible for the hydrogen exchange in the α-position of leucine, while the exchange in the β-position is in all probability a consequence of the keto–enol tautomerism of the ketoacid (XXVI):





Numerous studies of the kinetics of hydrogen exchange in peptides and proteins (see, for example, Refs. 37–41) as well as polyamides, treated as models of protein[41–44], indicate, in the way already mentioned above for polynucleotides, a considerable influence of the polymer matrix (particularly a protein matrix) on the nature of the transition state and the exchange mechanism. The rate of exchange is determined by the steric accessibility of various sections of the protein molecule to the solvent and is a minimum for the most ordered structures. It has been shown for collagen[45] that, as a result of the rupture of intramolecular hydrogen bonds, the exchange with D_2O is accelerated.

The hydrogen atoms in aromatic compounds are also capable of isotope exchange in an alkaline medium (NaOT or KOT solutions in HTO or in HTO–DMF, MeONa in MeOT, and KNT_2 in liquid NT_3).[46] The exchange is promoted by the presence of methoxy-groups and particularly phenolic hydroxy-groups as substituents in the aromatic ring, which has been used to introduce tritium into the *ortho*- and *para*-positions relative to the hydroxy-group in phenolic aminoacids[47] and in phenolic alkaloids related to morphine[48–51]. Heteroaromatic compounds and their hydro-derivatives also exchange under analogous conditions; the exchange is most effective in liquid NT_3,[46,51] but experimental difficulties in studies using this solvent limit its practical application. The exchange involving nitrogen-containing heterocycles is greatly accelerated when powerful electron-accepting substituents (oxide oxygen or a nitroso-group) are present at the nitrogen atom[46,52,53]. The mechanism of the exchange involves two stages—the formation of a carbanion and its subsequent interaction with the labelled medium; both the first stage (in the exchange of methyl hydrogen atoms in ethyl-substituted heterocycles)[53] and the second stage (in the exchange of hydrogen at $C_{(3)}$ in 2-substituted indoles)[54,55] can be rate-limiting.

2. Acid Catalysis

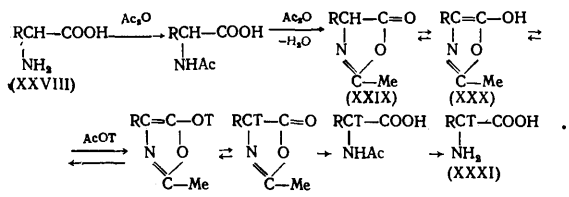
In the homogeneous acid catalysis of hydrogen isotope exchange the intermediate carbonium ion plays the same role as the carbanion in base catalysis (see above). The carbonium ion can be formed either as a result of the abstraction of a hydride ion from the molecule or (more often) as a result of the addition of T^+ or D^+ to an unsaturated carbon atom. The latter version obtains in numerous hydrogen exchange reactions in aromatic systems. The acid agents employed (see the review of Burrish et al.[56]) are strong protic acids (sulphuric, phosphoric, perchloric, and trifluoroacetic), weak acids (for example acetic), Lewis acids ($AlCl_3$, $AlBr_3$, and $EtAlCl_2$), and the complex $H_2TPO_4.BF_3$ (the so-called Yavorsky reagent[57]).

Virtually all these agents have been used successfully to introduce the tritium label into aromatic and heteroaromatic compounds, although in certain cases, involving $HTSO_4$ at elevated temperatures, undesirable side reactions do occur. Howver, tritium has been introduced into *l*-phenylalanine and its *p*-nitrophenyl ester with high yields on heating (90° to 100 °C, 48–72 h) with dilute $HTSO_4$ (or formed from SO_3 and HTO), approximately 95% of the incorporated tritium being contained in the benzene ring and approximately 5% in the β-position[58]. The exchange is accompanied by a slight (<4%) racemisation; the value of a for the preparations obtained amounts to several μc $mmol^{-1}$.

In order to obtain other labelled tritiated aromatic aminoacids with a of the same order of magnitude, 3–4 *N* solutions of TCl in HTO are most frequently used (heating at 40–90 °C). Under these conditions, 3-hydroxy-*l*-kynurenine exchanges only in the benzene ring[59] and *l*-5-hydroxytryptophan exchanges in the 2-, 4-, and 6-positions in the indole ring[60,61], while the side chains are unaffected and the exchange does not involve racemisation. On raising the temperature (100 °C, several hours), it is possible to achieve the exchange of all the hydrogen atoms in the benzene ring of L-5-hydroxytryptophan[60] and of the hydrogen atom in the 3- and 5-positions of tyrosine and in the 2-, 5-, and 6-positions of 3,4-dihydroxyphenylalanine[47], while it has been shown with the aid of deuterium that in tryptophan[62] the hydrogen atoms in the 2- and 6-positions exchange rapidly and those in the 4-, 5-, and 7-positions exchange slowly only in trifluoroacetic acid. Like tyrosine, 4-aminobenzoic acid also exchanges in the 3- and 5-positions on heating with 3 *N* TCl in HTO (90 °C, 36 h). This preparation with $a = 2.5$ μc mg^{-1} has been used[63] to synthesise the tritium-labelled 4-methylpiperazide of 4-[*N*-(7-trifluoromethylquinolinyl)amino]benzoic acid, which exerts an effect on the central nervous system.

It has also been shown with the aid of deuterium that an acid medium (DCl in D_2O or AcOD) is suitable for the introduction of the label not only into the benzene ring but also into non-benzenoid aromatic and heteroaromatic natural products—azulenes[64,65], indoles (in the 3-position)[66], chlorophylls[67], and porphyrins[68]. In the same medium [DCl (TCl) in AcOD (AcOT) at 120 °C] the α-hydrogen atoms of carboxylic and aminoacids exchange[69] and also certain aliphatic acids, for example stearic[70], exchange with HTO (130 °C, 48 h, a reaching 1 c g^{-1} after washing out the labile tritium) without any extra acid additives.

As regards tritium-containing aminoacids (XXXI), the latter are obtained most effectively by refluxing the Ac_2O in AcOT (the reagent is prepared by adding an excess of Ac_2O to HTO) and subsequent treatment with HTO.[71–74] In this case the hydrogen atom in the α-position exchanges exclusively (or almost exclusively) and the exchange is accompanied by racemisation and does in fact occur for the aminoacid (XXVIII) itself but involves the intermediate azlactone (XXIX), which is converted into the tautomeric form (XXX):



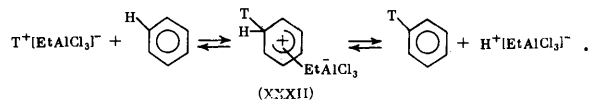
Despite the fact that DL-aminoacids are obtained by this method, in combination with enzymatic resolution of racemates it can be used also to obtain labelled L-aminoacids[73]. An analogous procedure (boiling with Ac_2O into AcOD followed by treatment with D_2O) has recently been proposed as a method for the introduction of deuterium into the α-position in aminoacids[75].

The use of the Yavorsky reagent (the complex $H_2TPO_4.BF_3$) as the tritiating agent for aromatic compounds and compounds containing tertiary hydrogen has a number of advantages (the exchange takes place even at room temperature and there are no side reactions, which leads to radiochemical purity of the products[57,76]); however, owing to the low values of a (at most tens of μc $mmol^{-1}$) attainable with its aid, it is hardly used for the preparation of labelled BAS. Insecticides (DDT, parathion, sevin, and their analogues)[77], tropine, and mescalin[78] are exceptions. Recently this list was extended by including insulin ($a \approx 6.5$ μc $mmol^{-1}$ [79] and also certain phenols ($a = 10–80$ μc $mmol^{-1}$), converted as a result of esterification into labelled hypolipidemic agents (including clofibrate)[80].

A modification of the Yavorsky reagent—the complex $AcOT.BF_3$ (prepared by the successive addition of a slight excess of Ac_2O and an equivalent amount of BF_3 to HTO)—was proposed from the very beginning[81] specifically for the introduction of the tritium label into BAS—aminoacids, peptides, proteins (α-lipoprotein, ribonucleoprotein, somatotropin, and insulin), and cholesterol. The exchange takes place under mild conditions (20–24 °C, approximately 20 h), but certain proteins (human albumin and ovalbumin) are

nevertheless denatured and the values of a attained do not exceed 150 μc g^{-1}.

Lewis acids ($AlCl_3$, $AlBr_3$, $MeAlCl_2$, $EtAlCl_2$, WCl_6, $SbCl_5$, and BBr_3) catalyse hydrogen isotope exchange mainly in aromatic compounds and their use for labelled BAS is therefore extremely limited. Best results have been achieved for polynuclear aromatic hydrocarbons—methylcholanthrene, 3,4-benzopyrene, and 9,10-dimethyl-1,2-benzanthracene, which are powerful carcinogens and are widely used in oncological research. After being kept with HTO and $AlCl_3$ in CS_2 for many days (14–50 days at 20 °C), these hydrocarbons are converted into the corresponding generally labelled compounds with $a \cong 20$–50 c mmol^{-1}.[82] The attempts to use $AlCl_3$ as the catalyst of the exchange between HTO and uracil, adenine, and glycine or its peptides (in CH_2Cl_2 at 80 °C) were less successful[83]. Among all the catalysts of this type, the most effective is apparently $EtAlCl_2$, in the presence of which full equilibrium between aromatic hydrocarbons is attained for benzene and its homologues and derivatives after only 30 min at 20 °C.[84] In this case the TCl formed as a rsult of the partial hydrolysis of the catalyst plays the role of a cocatalyst: the strong acid $T^+[EtAlCl_3]$, obtained from TCl and $EtAlCl_2$, adds to the aromatic ring to form the complex (XXXII). The equilibrium between the hydrocarbon, the acid, and the complex is responsible for the hydrogen exchange[85]:



(XXXII)

The catalysis by other Lewis acids proceeds via a similar mechanism. It has been suggested[86] that the HTO–$EtAlCl_2$ system be used for the introduction of tritium into alkanes and cycloalkanes (including steroids) containing at least one tertiary hydrogen atom. However, in order to attain satisfactory values of a, a fairly high temperature (96 °C) is necessary, which also promotes skeletal isomerisation reactions in the intermediate carbonium ion, which leads to the formation of labelled side products. For steroids or other BAS, this method has not found any serious applications.

In catalysis by Lewis acids of the reaction involving the exchange of H for D the experimental procedure is simplified, since deuterated aromatic hydrocarbons (usually C_6D_6) can be employed as the labelled medium[84,87].

The hydrogen isotope exchange in an acidic (sometimes weakly acidic) medium, initiated by various types of radiation (ultraviolet radiation[88–92], γ-radiation[93,94], and the intrinsic radiation of HTO with a high value of a [95,96]), constitutes a special variety of homogeneous acid catalysis. Such exchange involves both aromatic[88–92] and aliphatic[93–96] compounds (particularly carbohydrates[94,95]); the initiation is facilitated by the addition to the medium of substances readily forming radicals—potassium iodide[89,90] and mercaptans[94]. In all cases radicals are formed as an intermediate stage: for aromatic compounds as a result of the addition of T· and for aliphatic compounds as a result of the abstraction of H·. For example, in the exchange between benzene and HTO in an acid medium in the presence of KI irradiation induces primarily the decomposition of the I^- ion into I· and a solvated electron[89]. The interaction of the latter with the cation H_2TO^+ leads to H_2O and T·, the addition of which to the benzene molecule with subsequent elimination of H from the radical [PhHT]· is responsible for the incorporation of tritium into the aromatic ring. In a weakly acid medium the solvated electrons can be captured by benzene molecules with formation of the anion $[PhH]^-$, which is converted into the radical [PhHT]· as a result of the interaction with the tritium-containing medium[90].

On the basis of published data, isotope exchange initiated by irradiation appears to be relatively unsuitable for the preparative synthesis of labelled BAS, mainly because of side reactions. Even for simple compounds, an inversion of configuration is observed as a consequence of the homolysis of the C–H bond of an asymmetric carbon atom. Thus the isotope exchange between (+)-tartaric acid and HTO initiated by γ-radiation leads to a 1 : 1 mixture of labelled (+)- and *meso*-tartaric acids, while a mixture of labelled *meso*- and (±)-tartaric acids is obtained from *meso*-tartaric acid under these conditions[93]. The exchange between HTO and *chiro*-inositol, initiated by the intrinsic radiation, leads similarly to the formation of tritiated *chiro*-, *myo*-, and *allo*-inositols (but not *muco*-inositol)[95]. The greater ease of exchange of the equatorial hydrogen atoms compared with the axial atoms was noted in this instance.

3. Catalysis by Transition Metal Salts

From the point of view of the synthesis of labelled BAS, the preparative value of the last of the varieties of homogeneous catalysis considered here—isotope exchange with HTO in the presence of soluble chloroplatinates (Na_2PtCl_4 and K_2PtCl_4)—is low. This exchange also proceeds in an acid medium (acetic acid is added to homogenise the solution, while hydrochloric acid prevents the precipitation of metallic platinum) and requires an increased temperature (from 50° to 130 °C).[97–101] The mechanism of the exchange involves the formation of a complex of the type of a π-complex from the substrate and the transition metal[98]. The method described is therefore effective primarily for the hydrogen atoms of an aromatic ring, polynuclear compounds (napthalene, anthracene, and phenanthrene) exchanging specifically in the β-position. A comparative study[102] has shown that catalysis by K_2PtCl_4 is preferable (requires a lower temperature and a shorter time) than heterogeneous catalysis of the exchange with the solvent in the presence of platinum for the introduction of the deuterium label into hexoestrol, oestrone, testosterone, and cholesterol.

The homogeneous catalysis by mercury(II) chloride of the isotope exchange between a nucleoside [2-acetamido-6-chloro-9-(2′-deoxy-3′,5′-di-*O*-*p*-toluyl-D-ribofuranosyl)-9*H*-purine] and tritium-containing aromatic solvents—benzene and toluene (refluxing for 0.5 h)—has also been described[103]. Under these comparatively mild conditions, the efficiency of the exchange is low (a for the labelled nucleoside is smaller by a factor of approximately 10^4 than for the initial solvent) and the incorporated tritium is distributed between the purine and the carbohydrate moieties of the nucleoside molecule in proportions of 84 : 16.

IV. HETEROGENEOUS CATALYSIS OF HYDROGEN ISOTOPE EXCHANGE

The methods for the homogeneous catalysis of isotope exchange examined above make it possible to obtain tritium-containing compounds with a high value of a (of the order of several tens of c mmol^{-1} or at least several c mmol^{-1}) in only a few cases. In contrast to these procedures, in heterogeneous catalysis such high values of a can be obtained much more readily which constitutes the main advantage of this group of methods. In heterogeneous catalysis of isotope exchange in solution, both tritium-containing solvents (usually water) and gaseous T_2 can serve as sources of tritium.

1. Exchange with Tritium-Containing Solvents

In this case the experimental procedure usually consists in prolonged heating of a mixture of the test substance, the tritium-containing solvent, and the catalyst. The method has come to be widely employed since the 1950s and a compilation of early studies on this problem (up to 1964) can be found in the first edition of Evans's monograph[104]. The method is nowadays widely used and one of the largest centres of isotope production in the world—the Radiochemical Centre in Amersham—uses it for the industrial manufacture of a wide variety of tritium-labelled compounds, including a large number of BAS.

Table 1. Biologically active substances labelled by the method of heterogeneous catalytic exchange with the solvent (catalyst—Pt black)*.

Substance	a of solvent**	t, °C	Time, h	Yield, %	a of product, μc mmol^{-1}
	Solvent—HTO				
DL-Alanine	1.8	140	16	30	1 130
Anisomycin	150	100	16		285
DL-Aspartic acid	1.35	130	15	68	466
DL-Valine	1.08	120	16	80	20
Vitamin B_{12}	80	140	20	50	4 804
Glycine	1.04	100	8.5	58	176
DL-Glutamic acid	1.8	130	15	15	74
Guanine	70	145	20	50	150
Guanosine	90	130	16	20	481
Deoxyguanosine	87	120	3	0.2	1 000
Deoxycytidine	70	130	16	0.4	1 527
DL-3,4-Dihydroxyphenylalanine	1.35	125	16	35	268
DL-Isoleucine	1.8	155	16	40	314
Isonicotinoylhydrazine	100	125	16	72	1 323
Coumarin	6.3	130	16	34	2 242
DL-Leucine	0.54	120	66	47	103
5-Methylcytosine	100	130	16	10	15 600
Nicotine	35	100	72	33	82
Pyridoxin	200	120	16	3	1 500
DL-Serine	1.44	130	15	60	138
Stilboestrol	10	140	5	42	295
DL-Tyrosine	1.35	150	17	48	102
DL-Tryptophan	1.44	100	18	28	685
DL-Phenylalanine	2.16	140	16	50	1 800
	Solvent—70% AcOT				
Adenine	67	130	14	70	439
Adenosine	63	110	8	5	680
Androstenedione	40	150	48	50	3400
1,2-Benzanthracene	150	150	16	40	655
3,4-Benzopyrene	25	160	16	64	451
Hypoxanthine	50	150	15	30	630
Deoxyadenosine	67	100	6.5	7	627
Deoxyuridine	33	100	5	20	385
9,10-Dimethyl-1,2-benzanthracene	30	150	16	50	3250
Inosine	50	100	20	8	642
Corticosterone acetate	38	130	16	32	1590
Caffeine	25	150	16	36	1280
2-Methylcholanthrene	225	145	16	14	3150
Orotic acid	250	140	15	65	115
Prednisolone	160	150	5	10	685
Progesterone	88	140	16	43	509
Theophylline	75	140	16	21	1480
Thymidine	100	170	15	20	8600
Uracil	50	155	16	50	482
Uridine	75	120	16	35	1008
Cholesterol	180	155	16	23	1620
Cytosine	40	100	20	40	300
Oestradiol	200	140	16	21	174
Oestrone	14	130	90	56	188

*Reaction mixture—0.2–0.5 g of substance with 50–100 wt.% of catalyst in 2–4 ml of solvent.

**The values for the exchange with aminoacids and coumarin are quoted in c mmol^{-1}; in all other cases they are expressed in c ml^{-1}.

In the exchange with the solvent the catalysts can be virtually all Group VIII metals—platinum, palladium, cobalt, nickel, ruthenium, rhodium, and iridium—which are prepared by reducing their salts with $NaBH_4$ or by reducing their oxides with T_2 (or D_2) [105–108] and are used as such (platinum black, palladium black, etc.) or on various carriers (silica gel, activated charcoal, Al_2O_3, $BaCO_3$, $CaCO_3$). In Amersham preference is given to the platinum catalyst[105], but a high efficiency of the nickel (Raney nickel) and chrome-nickel catalysts has also been reported[109,110]. In choosing the catalyst, account must be taken of its influence on the intramolecular distribution of the added tritium (as a rule, platinum and palladium are less specific; for further details, see below) and also the fact that arsenic, sulphur, and certain nitrogen-containing compounds poison many (but not all) catalysts.

The most common medium in heterogeneous catalytic exchange in solution is HTO itself and also a 70 : 30 mixture of AcOT and HTO. In order to attain high values of a, a temperature of approximately 120–150 °C and a treatment time ranging from 2 to 20 h (in rare instances significantly longer—up to 65–90 h) are required. Under these conditions, tritium is introduced into the majority of low-molecular-weight BAS. The side reactions can be the migration of the Δ-bond (in unsaturated compounds), partial hydrolytic cleavage, and (when AcOT is used) acetylation, but the labelled side products have approximately the same value of a as the main compound. As a result, their separation does not as a rule present a specially difficult problem (which is an advantage over the Wilzbach method and its modifications). The activity a of the products naturally depends on the molar activity of the solvent and reaches up to 80% of the latter under most favourable conditions.

Table 1 presents specific results achieved by the Radiochemical Centre in the preparation by the method described (with platinum black as the catalyst) of certain low-molecular-weight BAS.[105] Evidently the ease of introduction of tritium into various compounds of even the same class (for example into aminoacids) is varied. In the majority of cases the exchange of the hydrogen in aromatic rings is easier than in aliphatic residues. One should also note that the values of a quoted in Table 1 for readily exchanging substances are by no means limiting values. Thus the synthesis of adenosine triphosphate with a = 23.3 c mmol^{-1} as a result of the platinum-catalysed exchange with HTO has been reported recently[21].

As regards the classes of BAS not mentioned in Table 1, the exchange with HTO in the presence of platinum (140 °C, 20–70 h) has been used to introduce tritium into terpenes (~2 μc mg^{-1});[111] the possibility of using the "self-activating" PtO_2 (HTO, 130 °C, 48 h) as a catalyst rather than platinum has been demonstrated for carbohydrates in relation to (−)-inositol (a = 3.39 μc mmol^{-1}).[112] However, Raney nickel, which catalyses the exchange between D_2O and α-methyl-D-mannopyranoside, β-methyl-D-galactopyranoside, 1,2-*O*-isopropylidene-α-glucofuranose, α,α-trehalose, melezitose, raffinose, and sucrose (100 °C, 10 h), is more promising for the introduction of a label into carbohydrates[109].

The principal disadvantages of the method under consideration are the use of very large amounts (up to 500 and more curies) of HTO and the relative severity of the exchange conditions. In order to overcome the first of these disadvantages, it has been suggested[113,114] that the labelled water required for the exchange be obtained by oxidising gaseous T_2 with a suspension of PtO_2 in AcOH, dioxan, or methanol in the apparatus where the exchange itself takes place; the exchange is catalysed by platinum formed on reduction of PtO_2, which makes it possible to obtain tritiated water with

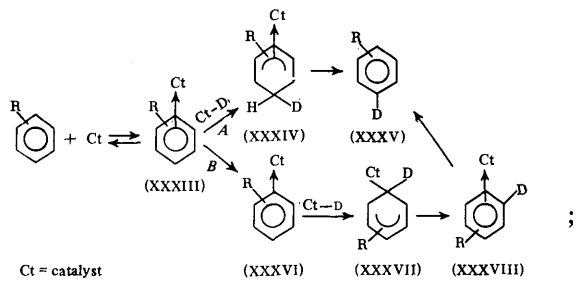
the maximum specific activity, to remove the excess T_2, and in many cases to eliminate the problem of the dissolution of the starting material. With the aid of this modification of the method, folic acid and uridine with $a \cong 1$–3 c mmol^{-1} were obtained (AcOH, 120 °C, 24 h),[113] while under milder conditions (dioxan or MeOH, ~20 °C, 4–24 h) geraniol, linalool, gibberelic acid, hydroxytetracyclin, and phenylalanine were synthesised with a ranging from 50 to 500 μc mmol^{-1}.[114]

The last example demonstrates that, as stated above, the attainment of a high value of a requires an increased temperature. This disadvantage of the method significantly restricts the range of BAS to which it can be applied, since biopolymers (particularly polypeptides and proteins) decompose on heating in most instances, while optically active aminoacids racemise. Thus, although L-phenylalanine exchanges with HTO at 30 °C in the presence of platinum without racemisation (since the side chain is not involved and more than 90% of the incorporated tritium is localised in the benzene ring), the overall degree of incorporation of tritium is small, while at 130 °C generally labelled DL-phenylalanine is obtained[115]. A high degree of racemisation (20–50% of the D-form) under the conditions of the exchange with HTO at 120–150 °C has also been noted[105] for L-tyrosine, L-tryptophan, and L-methionine, while the degree of racemisation in the case of arginine, lysine, and leucine did not exceed 5% and the values of a were below 200 μc mmol^{-1}.

In addition it has been shown with the aid of deuterium that the hydrogen isotope exchange involving the aromatic ring and catalysed by platinum under mild conditions is observed for phenylalanine and its tripeptide, but hardly occurs for the phenylalanyl and tyrosyl residues in proteins such as lysozyme and ribonuclease (the possible causes are steric hindrance to the adsorption of these residues on the catalyst or irreversible poisoning of the catalyst by the protein)[116]. Nevertheless, it is most likely that conformational factors play a decisive role, because, after prolonged treatment (40 °C, 72 h) with 35 c HTO and platinum black, it was possible to obtain labelled ribonuclease with $a = 17.3$ c mmol^{-1}; the bulk of the tritium was present in the valine, lysine, arginine, and glutamic acid residues[117]. Under the same conditions, tritium was introduced into oxidised ribonuclease much less effectively ($a = 0.2$ c mmol^{-1})—mainly into histidine and sulphur-containing and aromatic aminoacid residues. Tritium-containing polypeptides—ochratoxins A, B, and C (yield 80%, a up to 3 c mmol^{-1})—have been obtained[118] with the aid of heterogeneous catalytic exchange with the solvent (a mixture of HTO and AcOT, platinum black, 80 °C), ochratoxin A being labelled mainly (to an extent greater than 80%) in the phenylalanyl residue[118].

One of the slight disadvantages of the method is the uncertainty in the predicted location of tritium in the labelled compound obtained. These compounds are referred to as generally labelled or indefinitely labelled (in contrast to specifically labelled and uniformly labelled). The intramolecular distribution of tritium depends on a number of factors (primarily on temperature and on the nature of the catalyst) and it has been stated[119] that the reproducibility of the results of studies of the intramolecular distribution are poorly reproducible. The influence of temperature on the localisation of tritium in phenylalanine was noted above but even in high-temperature exchange (135 °C, 18 h), accompanied by complete racemisation, tritium is not distributed uniformly between the side chain and the aromatic ring, but is concentrated mainly in the latter (in proportions of 27 : 73).[120] A definite selectivity also obtains in a number of other instances: in catalysis by platinum black uracil exchanges with HTO mainly the hydrogen atoms in the 5- and 6-positions[121]; the exchange between (−)-inositol and HTO in the presence of PtO_2 leads to preferential (to the extent of 92.5%) inclusion of tritium in the 1- and 6-positions[117]; the exchange of sugars with D_2O in the presence of nickel takes place at $C_{(5)}$ and $C_{(6)}$ much faster than at $C_{(2)}$ and $C_{(3)}$;[109] cobalt catalyses the exchange of hydrogen in heterocycles exclusively in the α-position[108]. Poisoning of the catalyst also influences the location of tritium: thus, when pyridine is added, the exchange between HTO or D_2O and alkylbenzenes catalysed by Pd/C is selectively inhibited in the *ortho*-position relative to the alkyl group[122].

As regards the mechanism of the heterogeneous catalysis of the exchange with the solvent, it has been found that the exchange on different catalysts takes place in different ways. In the most common exchange of aromatic compounds in the presence of platinum it has been suggested[123] (on the basis of the results of a study of deuterium exchange) that a π-complex (XXXIII) is formed in the first stage. The complex then either interacts with the deuterium (tritium) sorbed on the catalyst (as a result of the dissociative chemisorption of water), being converted via a transition state (XXXIV) into the labelled compound (XXXV) ("associative mechanism"; A) or ("dissociative mechanism"; B) is first converted into a σ-complex (XXXVI), which reacts slowly with the deuterium (tritium) sorbed on the catalyst to form the addition product (XXXVII). The labelled compound (XXXV) is obtained from the latter via the labelled π-complex (XXXVIII). The dissociative mechanism is believed to be more probable[123–125]:



2. Exchange with Gaseous Tritium

The use of gaseous T_2 as a source of tritium in the heterogeneous catalysis of hydrogen isotope exchange in solution has a number of advantages over the use of tritium-containing solvents (see reviews[105,126]). These include primarily the possibility of carrying out the exchange at the usual temperature and of obtaining over a period of only several hours labelled compounds with $a \cong 1$–10 c mmol^{-1} (and sometimes even higher). The method consists in stirring a solution of 10–50 mg of the test substance in several millilitres of a suitable solvent in an atmosphere of 10–25 c T_2 in the presence of a catalyst. The overall radioactivity in the experiment is thus approximately ten times lower than in the exchange with a solvent. The exchange is faster if the pressure of T_2 is equal to the atmospheric pressure, but this condition is not obligatory and sometimes high values of a are attained in several hours even at a pressure of 160 mmHg.[127] The reaction is carried out in a special vacuum system (for a detailed description of such vacuum apparatus tested in practice, see Mikhailov et al.[128]).

The influence of various factors (solvent, temperature, and catalyst) on the exchange with T_2 has been inadequately investigated, but it has been established that there are apparently no special limitations as regards the choice of the solvent. Both organic solvents (dioxan, methanol,

hexane, CCl_4, CS_2, acetic acid, etc.)[129,130] and water or aqueous buffered solutions at neutral or alkaline pH are used[131]. The isotope exchange between T_2 and organic solvents is slight under these conditions; it increases slowly in the series dioxan < tetrahydrofuran < ethyl acetate[132], but even ethyl acetate can be used successfully (for example, in the exchange between T_2 and cholesterol)[133]. Satisfactory results are obtained even at 20–25 °C, but there is evidence[130,134] that an increase of temperature to 60–65 °C makes it possible to increase a of the exchange products by a factor of 2–3.

Palladium and platinum or their oxides (in the latter case the exchange is preceded by the reduction of the oxides to the metals) are most frequently used as catalysts[131,134] either as such or deposited on various carriers ($CaCO_3$, $BaSO_4$, activated charcoal, and Al_2O_3; in addition nickel[135], Rh/Al_2O_3,[136] and certain other catalysts are also employed). The nature of the carrier is not important[137,138], although in certain cases the use of $CaCO_3$ suppressed side reactions[138]. The method of activation of the catalyst is more important: in the preliminary reduction of PdO or PtO_2 by H_2 (instead of T_2) the value of a of the products decreases by a factor of 30–60.[129,134]

Table 2. Compounds labelled with the aid of heterogenous catalytic exchange with T_2 in solution[131] (catalyst—$PdO/BaSO_4$)*.

Compound	pH of solution	Time, h	Yield, μc	a, c mmol^{-1}
Adenosine	8.2	2	660	11.2
Adenosine monophosphate	10	16	295	—
Adenosine cyclic 3',5'-diphosphate**	10	16	290	28.3
Adenosine triphosphate	8	16	84	13.0
Deoxyadenosine triphosphate	10	16	250	9.6
Inosine monophosphate	8	0,33	195	4.9
Guanosine triphosphate	8.2	0,5	28	1.6
Puromycin	8	0,5	28	3.75

*10–30 mg of substance with a fourfold–fivefold excess (by weight) of catalyst in 1.5–2.5 ml of phosphate buffer (atmosphere of 10 c T_2).
**In an atmosphere of 25 c T_2.

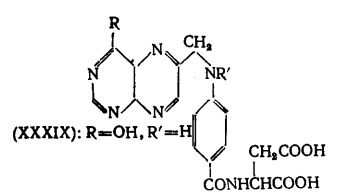
Heterogeneous exchange with T_2 in solution has been used successfully to introduce the label into carbohydrates, nucleotides, steroids, and certain other BAS containing aromatic or heteroaromatic rings and in most cases the selectivity (or even specificity) of the exchange was noted. D-glucose-1-*t* is obtained very readily (~20 °C, 1 h) as a result of the exchange with T_2 in 0.1 M phosphate buffer in the presence of $PdO/BaSO_4$ (a = 5.4 c mmol^{-1}).[131] Other aldoses—L- and D-arabinoses, L- and D-fucoses, D-ribose, maltose, and lactose—exchange just as specifically. The presence of the aldehyde group is an obligatory condition for the exchange: under analogous conditions, it is not possible to introduce tritium into sorbitol, α- and β-methyl glucosides, or trehalose[131]. Tritium has been introduced by the above method also into more complex compounds containing carbohydrate residues: platinum catalyses the exchange of T_2 with the aminoglycoside antibiotic sagamicin[139] and 30% Pd/C catalyses the exchange with heparin [water–ethylcarbitol (monoethyl ether of diethylene glycol), ~20 °C, 48 h];[140] nucleosides and nucleotides as well as the antibiotic puromycin with a high value of a and a radiochemical purity of 90–98% have been obtained by exchange in the presence of $PdO/BaSO_4$ in phosphate buffer (Table 2).[131]

Hydrogen in the 8-position exchanges most readily in purine derivatives[131]; among pyrimidines, tritium is introduced selectively in the 6-position in 5-hydroxyuracil and 5-aminouracil (5% $Pd/BaSO_4$, water, 23 °C, 3 h) with a = 0.35 and 2.36 c mmol^{-1} respectively[127].

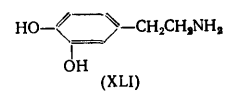
It is noteworthy that tritium introduced into galactosylceramide and glucosylceramide (10 c T_2, 10% Pd/C, on chloroform–methanol in the presence of pyridine, ~20 °C) is almost fully localised (to an extent greater than 98%) in the sphingolipid part of the molecule and of that more than 80% is in the aliphatic acid residue[141].

The exchange of T_2 with steroids—cholesterol (a up to 1 c mmol^{-1})[133,142] and oestrogens (oestrone, oestriol, and oestradiol; $a \cong 1.5$ c mmol^{-1})[134,143]—is catalysed by palladium or platinum, best results being obtained using benzoates in organic solvents (ethyl acetate or dioxan) with subsequent hydrolysis.

Among aminoacids, L-phenylalanine exchanges very readily with T_2 in solution in the presence of PtO_2 [134] or $PdO/BaSO_4$ [131]. In the latter case (phosphate buffer, pH 7, 20 °C, 1 h) a > 1 c mmol^{-1} was attained. The exchange is not accompanied by racemisation and involves almost exclusively (to an extent greater than 95%) the benzyl CH_2 group (the 3-position). Under analogous conditions, it was possible to obtain labelled L-alanine with a equal to only 10 μc mmol^{-1}.[131] This example illustrates strikingly the extreme ease of the exchange of the benzyl hydrogen atoms in the α-position, which has been confirmed also in other cases[129] and has been used to introduce tritium into a series of BAS containing benzyl or analogous groups. These compounds include, for example, folic acid (XXXIX), in which more than 60% of the incorporated tritium is localised in the 9-position after exchange with T_2 (10% Pd/CaO_3, 4 *N* KOH, ~20 °C, 1 h, a = 30–36 c mmol^{-1}), and 2-(3,4-dihydroxyphenyl)ethylamine (dopamine) (XLI), which belongs to the class of catecholamines, where more than 90% of the tritium label is introduced into the 2-position of the side chain after exchange with T_2 ($PdO/BaSO_4$, phosphate buffer, ~20 °C, 2 h, $a \cong 1$ c mmol^{-1}).[131] It is of interest to note that a compound related to folic acid—the medicinal preparation methotrexate (XL)—contains only 30% of the incorporated tritium in the 9-position (the conditions of the exchange were the same as for folic acid), evidently due to steric hindrance caused by the neighbouring methyl group[144]:



(XL): R=NH₂, R′=Me.



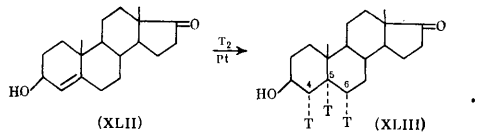
(XLI)

5-(3-Methylaminopropyl)- and 5-(3-dimethylaminopropyl)-10,11-dihydro-5*H*-dibenzo[*d*,*f*]azepins (the medicinal preparations desipramin and imipramin) as well as 5-(3-methylaminopropylidene)- and 5-(3-dimethylaminopropylidene-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclopentenes (the medicinal preparations nortriptyline and amitriptyline), which exhibit a powerful antidepressant activity, exchange with T_2 (PdO, methanol, ~20 °C, 45 min, a = 45, 15, 2, and 1.7 c mmol^{-1} respectively) almost exclusively at the methylene group located between the two aromatic rings[145]. Among other labelled medicinal substances obtained by exchange with T_2 and

exhibiting a high value of a, mention should be made of DL-propranol (PtdO, dioxan, 4.5 h, yields 37%, $a = 27.3$ c $mmol^{-1}$)[146] and 1-(1-phenylcyclohexyl)piperidine (the medicinal preparation phencyclidine) (PdO, methanol, yield 25%, $a = 4$ c $mmol^{-1}$).[147]

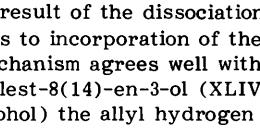
The number of biologically active substances which can be selected for the introduction of the tritium label by exchange with T_2 in solution is limited by the side reduction of certain groups and by the saturation of multiple bonds. Thus the attempt to introduce tritium into uridine by the above method ($PdO/BaSO_4$, phosphate buffer, 1 h) led only to dihydrouridine-5,6-*t*.[131] However these limitations are not absolute: for example, the exchange of aldoses mentioned above is not accompanied by the reduction of the aldehyde group. As regards unsaturated compounds, the saturation and isotope exchange of the latter proceed competitively and depend markedly on the conditions (catalyst and temperature). Thus the activation energy for the exchange involving cyclohexene in the presence of $Rh(PPh_3)_3Cl$ (homogeneous catalyst) is higher than for saturation and the latter is the main process at 30 °C, but at 60 °C the exchange proceeds more readily[148].

In the isotope exchange between T_2 and tricyclic antidepressants (see above) in the presence of palladium (from PdO) the degree of retention of the double bond is much greater than in the presence of PtO_2 or $PdO/BaSO_4$. Even better results are achieved when the stages involving the reduction of PdO to palladium and the exchange with antidepressants are separated and are carried out consecutively[145]. In the platinum-catalysed reduction of 3β-hydroxyandrost-4-en-17-one (XLII) by tritium the saturation and isotope exchange also proceeds simultaneously: in the labelled 3β-hydroxyandrostan-17-one (XLIII) obtained the tritium is distributed between the 4α-, 5α-, and 6α-positions in the proportions 37 : 43 : 20:[149]



(XLII) (XLIII)

As in heterogeneous catalysis of the exchange with the solvent, the mechanism of the exchange with gaseous T_2 (or D_2) is different for different catalysts (see, for example, Rudakov et al.[150]). In particular, for substituted aromatic compounds, chemisorption on the surface of the platinum or palladium catalysts in the form of π-complexes has been postulated[151,152], while in the case of the nickel catalyst the formation of σ,π-complexes is more likely[135]. The mechanism of the exchange with T_2 in aqueous media cannot be regarded as finally established; it has only been demonstrated that the substrate exchanges directly with T_2 and not with water[131]. In the discussion of the ionic and radical versions of this mechanism preference was given to the latter[131], which presupposes the homolysis of the C–H bond in the substrate RH in the first stage with formation of an intermediate free radical, adsorbed on the catalyst surface. This radical then interacts with the T atoms obtained as a result of the dissociation of T_2 on the catalyst, which leads to incorporation of the tritium in the substrate. This mechanism agrees well with, for example, the finding that cholest-8(14)-en-3-ol (XLIV) exchanges with D_2 (Pd catalyst, alcohol) the allyl hydrogen atoms at $C_{(7)}$ and and $C_{(15)}$. Evidently these most mobile atoms are split off with formation of an intermediate π-allyl complex[152]:



(XLIV)

V. CATALYTIC DEHALOGENATION

The method used for catalytic dehalogenation (stirring of the solution of the test substance in an atmosphere of gaseous T_2 in the presence of the catalyst) is identical with the method for heterogeneous exchange with T_2 (and also with that for catalytic reduction by T_2); in essence, catalytic dehalogenation differs from exchange by the fact that the T atom replaces a halogen atom rather than a hydrogen atom in the substrate molecule. We thus have the chemical reaction $RX + T_2 \rightarrow RT + TX$ and catalytic dehalogenation is accordingly one of the synthetic methods for the preparation of tritium-containing compounds. However, as already stated above, the inclusion of this method in the present review is justified, firstly, by the fact that it is most general for the synthesis of labelled BAS of different classes, and, secondly, because of its evident theoretical and practical similarity to exchange methods.

The advantages of the catalytic dehalogenation method are fairly clear. In the first place it makes it possible to obtain compounds with a high value of a and in many cases close to the theoretical value (29 c $mmol^{-1}$) corresponding to the complete substitution of one halogen atom by tritium. It is very significant that catalytic dehalogenation proceeds under very mild conditions (even at temperatures approximately in the range 0–5 °C and at a T_2 pressure of approximately 150–200 mmHg) and goes almost to completion in several hours. This can be explained by the greater thermodynamic ease of substitution of a halogen by T compared with substitution of H by T and by the fact that, owing to the smaller carbon–halogen bond dissociation energies compared with the C–H dissociation energies, the activation energy for dehalogenation is lower than for the isotope exchange of H for T. An important advantage is also the specificity of the introduction of the tritium label, determined by the position of the halogen in the molecule of the initial halogen-containing compound. However one should note the side reactions—isotope exchange and saturation of multiple bonds—can infringe the specificity and in certain cases (which are admittedly very few) the infringement can be very considerable[153–155].

The formation, together with the labelled compound, of tritiated hydrogen halides TX, which are catalytic poisons, can be included among the disadvantages of the method. In order to bind these poisons, KOH, NaOH, NH_3, Et_3N or $BaCO_3$ are added to the solution, which also displaces the equilibrium, accelerates the dehalogenation, and suppresses side reactions. The necessary initial halogen-substituted compounds are in most cases fairly readily available.

As already mentioned, the experimental conditions for catalytic dehalogenation are almost the same as in the isotope exchange with T_2. The amounts of T_2 used vary from several curies at pressures ranging from 100 to 760 mmHg. The range of solvents employed is very wide—aqueous alkalis, ethanol, methanol, dioxan, DMF etc. (water and alkaline agents enumerated above are added to the organic solvents when necessary).

Palladium (in the form of a black or on various carriers—activated charcoal, $CaCO_3$, $BaSO_4$, and Al_2O_3) is most often used as the catalyst; more rarely employed are platinum, nickel (Raney catalyst), and rhodium and more rarely still—osmium, iridium, and ruthenium. It is recommended that catalysts on carriers be employed, since this increases the active surface area and decreases the risk of poisoning of the catalyst. Satisfactory results are obtained when Pd/C and $Rh/CaCO_3$ or Rh/Al_2O_3 are used simultaneously for the dehalogenation of peptides and proteins[155–161]. The ease of substitution of a halogen by tritium decreases in the sequence I > Br > Cl > F in conformity with the increase of the carbon–halogen bond strength. It is therefore preferred to ha-

with the corresponding iodides, particularly since even debromination sometimes proceeds unsatisfactorily[157], although, for example, 5-bromonicotinic acid is converted into labelled nicotinic acid in 94% yield (5% $Pd/CaCO_3$, tetrahydrofuran, in the presence of $BaCO_3$, 20 °C, 8 h).[162] However, in general the rate of reductive deiodination is several times greater than that of debromination (in the series of halogenobenzenes at approximately 20 °C, in the dark, and in the absence of a catalyst by a factor of 5.5) [163] and exceeds even more the rate of dechlorination and defluorination. Thus the homolytic dissociation of the carbon–halogen bond is the rate-limiting stage of the reaction and as a result of this it is in many instances possible to achieve the selective introduction of tritium into polyhalogeno-compounds[163–165].

Although catalytic dehalogenation has been used successfully for the introduction of the tritium label in virtually all classes of BAS, the method is most valuable in the preparation of labelled aminoacids, peptides, proteins, nucleotides, nucleosides, and nucleic bases. Catalytic dehalogenation is the main method for the synthesis of all aromatic aminoacids specifically labelled in the aromatic ring and having a high value of a (Table 3). In all cases dehalogenation is not accompanied by racemisation and leads to compounds with a high radiochemical purity. Hydrogenolysis in an atmosphere of pure T_2 yielded aminoacids with high values of a [for example, 14 c mmol^{-1} for L-tyrosine-3-t;[166,168] in other cases a mixture of T_2 and H_2 was used[167,170]].

Table 3. Labelled aminoacids obtained by catalytic dehalogenation.

Aminoacid	Initial halogen-containing compound	Catalyst	Medium	Chemical yield, %	Refs.
L-Phenylalanine-2,4-t_2	L-2,4-dibromophenylalanine	$Pd/CaCO_3$	aqueous ethanol	90–100	166
3,4-Dihydroxyphenylalanine-2,5,6-t_3	methyl ester of *O,O'*, *N*-triacetyl-2,5,6-tribromo-3,4-dihydroxyphenylalanine	Pd/C	dioxan (Et_3N)	54	167
3,4-Dihydroxyphenylalanine-2,5,6-t_3	2,5,6-tribromo-3,4-dihydroxyphenylalanine	$Pd/CaCO_3$	aqueous ethanol (KOH)	90–100	166
3,4-Dihydroxyphenylalanine-6-t	methyl ester of *O,O'*, *N*-triacetyl-6-bromo-3,4-dihydroxyphenylalanine	Pd/C	dioxan (Et_3N)	72	167
L-Tyrosine-3-t	3-iodo-L-tyrosine	10% Pd/C	aqueous methanol (KOH)	about 90	168
L-Tyrosine-3-t	3-iodo-L-tyrosine	$Pd/CaCO_3$	aqueous ethanol	90–100	166
L-Tyrosine-3,5-t	3,5-di-iodo-L-tyrosine	$Pd/CaCO_3$	aqueous ethanol	90–100	166
L-Tyrosine-3,5-t_2	3,5-di-iodo-L-tyrosine	Raney Ni	water (NaOH)	90–100	169
L-Tyrosine-3,5-t_2	3,5-di-iodo-L-tyrosine	Raney Ni	water (NaOH)	–	169
DL-Tryptophan-5-t	5-bromo-DL-tryptophan	10% Pd/C	water (KOH)	–	170
DL-Tryptophan-5-t	5-bromo-DL-tryptophan	$Pd/CaCO_3$	aqueous ethanol	90–100	166
DL-Tryptophan-4-t	4-chloro-DL-tryptophan	10% Pd/C	water (KOH)	–	170
L-Histidine-2,5-t_2	2,5-di-iodo-L-histidine	$Pd/CaCO_3$	aqueous ethanol (KOH)	–	166

The halogen can be substituted by tritium in the same way not only in the aromatic aminoacids themselves but also in their residues forming part of the composition of peptides and proteins. The interest of investigators was concentrated mainly on labelled peptide hormones (oxytocin, vasopressin, angiotensin (II), corticotropin, and α-melanotropin) and their analogues, for which values a of the order of several tens of c mmol^{-1} were attained. The results are presented in Table 4, which shows that the method is suitable for peptide molecules of different sizes (from 3 to 61 aminoacid residues). In all cases the dehalogenation was carried out at room temperature and almost all the labelled compounds of the peptide-protein type enumerated in Table 4 were obtained from iodine-containing precursors, i.e. peptides incorporating 3,5-di-iodotyrosine or 4-iodophenylalanine. The only exceptions are compounds Nos.3–6, which were synthesised from brominated precursors (containing 3,5-dibromotyrosine) or chlorinated precursors (containing 4-chlorophenylalanine). In one case (No.12) acetamido-D-alanyl(4-amino-3,5-di-iodo)-L-phenylalanine was dehalogenated and not the halogeno-analogue of the labelled peptide, the resulting tritium-containing dipeptide being converted into the labelled analogue of α-melanotropin by the usual methods of peptide synthesis.

The halogen is introduced into the initial halogenopeptides by various methods. Peptide synthesis makes it possible to obtain from a halogenoaminoacid halogenopeptides with a fixed position of the halogen, which is known exactly. The need for halogenopeptides of this kind stimulated the development of peptide syntheses from 3,5-di-iodo-L-tyrosine[178]. Another method consists in the treatment of the peptide (or of one of its synthetic precursors) with I_2 in a chloroform–methanol–water mixture (iodination of tyrosine residues in the 3- and 5-positions in the benzene ring)[176] or with iodine chloride, which iodinates the tyrosine ring or the histidine side chain depending on the conditions[159].

Catalytic dehalogenation is used very widely (particularly in recent times) for the synthesis of tritium-labelled nucleic bases, nucleosides, and their monophosphates. The label is introduced both into various positions of the nucleus of the base (usually with the aid of debromination) and into the methyl group (with the aid of dechlorination); for the compounds obtained, a varies in the range 5–25 c mmol^{-1} (Table 5).

Despite the fact that the conversion of the labelled bases into labelled nucleosides and their phosphates does not give rise to serious difficulties, it is frequently preferred to obtain the latter directly by the catalytic dehalogenation of the corresponding bromo-compounds. The same catalysts are used as a rule ($Pd/BaSO_4$, Pd/C) and the solvent usually consists of aqueous solutions of alkalis, the same values of a being attained (5–25 c mmol^{-1}). Adenosine-8-t,[179,188–190] guanosine-8-t,[189,190] inosine-8-t,[189] uridine-5-t,[179–181] 2-deoxyuridine-5-t,[179,180] cytidine-5-t,[181] adenosine monophosphate-8-t,[170,191,192] adenosine cyclic phosphate-8-t,[179,193] and uridine monophosphate-5-t [179] have been obtained in this way, but the yields did not exceed 50–60% owing to the reduced reactivity of the initial bromine-containing compounds. The latter is apparently determined by the existence in solution of a secondary structure stabilised by intramolecular forces[179]. The weakening of this stabilisation increases both the yield and the value of a of the labelled nucleosides and nucleoside phosphates obtained.

In order to convert the labelled monophosphates into labelled triphosphates, enzymatic phosphorylation is used. As in the case of peptides, the manufacture of tritium-containing nucleoside phosphates stimulated the development of methods for the synthesis of the monophosphates of the corresponding bromonucleosides[194].

Table 4. Labelled peptides and proteins obtained by catalytic dehalogenation.

No.	Substance	*n**	Labelled aminoacid residue	Catalyst	Medium	Yield, %	*a*, c mmol^{-1}	Refs.
1	Thyroliberin (releasing factor of thyrotropine)	3	histidine	Pd/Al_2O_3	phosphate buffer (pH 7.3)	–	60	171
2	Angiotensin II	8	tyrosine	5% $Pd/CaCO_3$	phosphate buffer	–	56.3	172
3	Asparagine^1-valine^5-angiotensin II	8	tyrosine-3,5-t_2	10% Pd/C	aqueous DMF (Et_3N)	–	2-3	173
4	Lysine^8-desglycineamide-vasopressin	8	tyrosine^2-3,5-t_2	Pd/Al_2O_3	acetic acid	–	–	174
5	Lysine^8-vasopressin	9	tyrosine^2-3,5-t_2	Pd/Al_2O_3	acetic acid	–	12	174
6	Lysine^8-vasopressin	9	phenylalanine^3-4-t	Pd/Al_2O_3	acetic acid	–	–	174
7	Lysine^8-vasopressin	9		10% Pd/Al_2O_3	phosphate buffer	–	10	175
8	Lysine^8-vasopressin	9	tyrosine^2-3,5-t_2	5% $Pd/CaCO_3$	aqueous methanol	–	25	176
9	Arginine^8-vasopressin	9	tyrosine-3,5-t_2	5% $Pd/CaCO_3$	aqueous methanol	–	17	176
10	Oxytocin	9	tyrosine-3,5-t_2	5% $Pd/CaCO_3$	methanol–ethyl acetate (1 : 1)	–	20	176
11	Oxytocin	9	tyrosine**	$Pd/CaCO_3$	phosphate buffer (pH 6.4)	–	35	177
12	D-alananine^1-4-azido-L-phenylalanine^7-norvalin^4-α-melanotropin	13	4-azidophenylalanine-3,5-t_2	Pd/C with $Rh/CaCO_3$	–	–	11	160
13	*N*-Bromoacetyl-D-alanine^1-glycine^3-norvaline^4-α-melanotropin	13	tyrosine^2-3,5-t_2	5% Pd/C with 5% $Rh/CaCO_3$	DMF	76	11-20	161
14	*N*-Diazoacetalglycine^1-norvaline^4-α-melanotropin	13	tyrosine^2-3,5-t_2	ditto	DMF	81	21-36	161
15	D-Serine^1-lysine^{17,18}-corticotropin-(1-18)-octadecapeptide	18	tyrosine^2-3,5-t_2	"	DMF	57	17	156
16	β-Corticotropin-(1-24)-tetracosapeptide (tetracosactrin, synacthen)	24	tyrosine^2-3,5-t_2	"	DMF	42	29	156
17	β-Corticotropin-(1-24)-tetracosapeptide	24	tyrosine^{23}-3,5-t_2	"	DMF	20	46	155
18	β-Corticotropin-(1-24)-tetracosapeptide	24	phenylalanine^7-4-t	"	DMF	18	27	157
19	Human corticotropin	39	tyrosine^{23}-3,5-t_2	"	DMF	30	25	158
20	α-Neurotoxin from *Naja nigricolis*	61	histidine	Pd-Rh/Al_2O_3	phosphate buffer (pH 7)		14	159

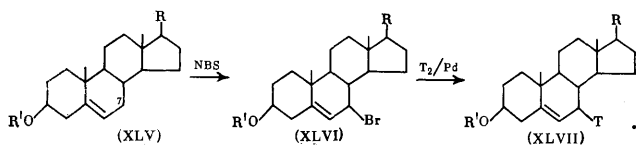
*Here *n* is the number of aminoacid residues.
**Tentatively.

Table 5. Labelled nucleic bases and their analogues obtained by catalytic dehalogenation.

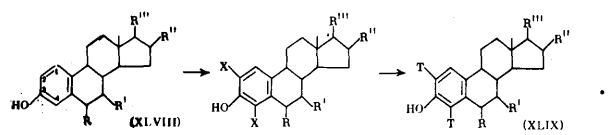
Labelled compound	Initial compound	Catalyst	Medium	Yield, %	*a*, c mmol^{-1}	Refs.
Uracil-5-*t*	5-bromouracil	$Pd/BaSO_4$	aqueous KOH	95-100	20-24	179
Uracil-5-*t*	5-iodouracil	Pt black			25	180
Uracil-5-*t*	5-iodouracil	5% $Pd/BaSO_4$	aqueous KOH	–	20	181
Uracil-6-*t*	6-bromo-2,4-dimethoxypyrimidine	5% $Pd/BaSO_4$	acetic anhydride	–	5-25	182
Cytosine-5-*t*	5-iodocytosine	5% $Pd/BaSO_4$	aqueous KOH	–	–	181
Thymine-methyl-*t*	5-(chloromethyl)uracil	10% $Pd/BaSO_4$	dioxan	70	15	154
Thymine-methyl-*t*	5-(hydroxymethyl)uracil	5% $Pd/BaSO_4$	aqueous acetic acid	77	15	154
5-Ethyluracil-4-*t*	4-chloro-5-ethyluracil	Pd/C	aqueous methanolic NaOH	85	–	183
5-Methylcytosine-methyl-*t*	5-(chloromethyl)-cytosine	PdO	dimethylacetamide	–	8	184
2,3-Dihydro-1,3-oxazine-2,5-dione-5-*t**	5-bromo-2,3-dihydro-1,3-oxazine-2,6-dione	5% $Pd/BaSO_4$	ethanol	64	11	185
Adenine-8-*t*	8-bromoadenine	Pd black	DMF	85-90	15	186, 187

*Synonym—3-oxauracil-5-*t*.

For steroids, the method of catalytic dehalogenation is particularly valuable, since it makes it possible to introduce the tritium label not only into a specific position and with retention of the Δ-bond, but also stereospecifically. Since steroids of type (XLV) are brominated by *N*-bromosuccinimide (NBS) exclusively in the 7α-position, the dehydrobromination of the resulting bromosteroids (XLVI) using Pd/C or $PdCaCO_3$ leads to 7α-labelled steroids (XLVII). Cholesterol-7α-*t*, pregnenolone-7α-*t*, and dehydroepiandrosterone-7α-*t* [195-198] were obtained by this method in yields exceeding 90% and with $a \cong 10$ c mmol^{-1}:[198]



Steroids (XLVIII) with an aromatic A ring, particularly the derivatives of oestradiol, are readily brominated (NBS) or iodinated (I_2 in aqueous methanol) in the 2- and 4-positions, which makes it possible to obtain subsequently by catalytic dehalogenation the steroid compounds (XLIX) labelled with tritium in these positions; oestradiol-2,4-t_2 (Raney Ni, aqueous NaOH),[169] oestriol-2,4-t_2 (Pd/C catalyst),[199] 16-oxo-oestradiol-2,4-t_2,[200] and isomeric oestra-1,3,5(10)-trienols-2,4-t_2 (5% Pd/Al_2O_3, ethyl acetate, $a = 15$–28 c mmol^{-1} [201]). The introduction of tritium into the 16-position in the 3α, 17α-dihydroxypregnane molecule has also been achieved by debromination (Pd/C catalyst):[202]



Vitamin K, labelled in the 6-position of the naphthoquinone nucleus (obtained from 6-bromo-2-methylnaphthaquinone with subsequent synthetic stages; (Pd/C, aqueous alcoholic NaOH, 5 °C),[203] α-tocopherol-(5-methyl-T) (obtained from 5-chloromethyl-α-tocopherol; Pd/C catalyst),[204] the antibiotic tetracycline-(7-T) (obtained from 7-chlorotetracycline, Pd/C, dioxan in the presence of tributylamine, $a = 5$ c mmol^{-1}),[205] the alkaloids papaverine (obtained from 6'-bromopapaverine; 10% Pd/C, dioxan containing Et_3N, $a = 43$ c mmol^{-1}; dehalogenation accompanied by exchange in methoxy-groups)[153] and *O*-benzoylecgonine-(benzoyl-2-T) [obtained from

O-(2-iodobenzoyl) ecgonine; Pd/C catalyst, $a = 21$ μc mg^{-1}],[206] the carcinogenic polycyclic aromatic hydrocarbon 7,8-dibenzoyloxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene, indefinitely labelled in the pyrene nucleus (obtained from a mixture of the corresponding bromopyrenes; Pd black, dioxan containing Et_3N, $a = 1.25$ *c* mmol^{-1}),[207] *N*-(2-imidazolidinylidene)-2,6-dichloroaniline-4-*t*—the medicinal preparation clonidine exhibiting a hypotensive activity (obtained from the corresponding 4-bromo-derivative; Pd/C, tetrahydrofuran, $a = 1.6$ c mmol^{-1}),[165] and the cardiac preparations practol [practolol? (Ed.of Translation)] and isopractol [isopractolol? (Ed.of Translation)] (obtained from 3,5-dibromo-4-hydroxyacetanilide with subsequent synthetic stages; 10% Pd/C, methanol containing Et_3N, yield 86%, $a = 20$ c mmol^{-1})[208] should be mentioned as examples of the application of the method of catalytic dehalogenation for the synthesis of labelled BAS of other types.

In conclusion one should note that catalytic dehalogenation is not the only method for the replacement of a halogen by tritium. For this purpose, the following procedures have been recommended in recent years: reduction with sodium amalgam in HTO,[209] reduction with zinc and CH_3COOT in ether [in the conversion of 17α-bromopregnenolone into pregnenolone-17α-*t*],[210] reduction with Zn–Cu alloy in organic solvents in the presence of HTO (in the introduction of deuterium into the 3-*exo*-position of camphor starting from 3-bromocamphor),[211] electrochemical reduction in HTO [in the synthesis of uracil-5-*t* and deoxyuracil-5-*t* from the corresponding 5-bromo-derivatives][212,213], and finally simple heating of certain 5-iodopyrimidines (orotic acid, uracil, cytosine, and their derivatives) in dimethyl sulphoxide containing 5% HTO.[214] However, in all the instances enumerated the activity *a* of the resulting preparations was appreciably lower than in catalytic dehalogenation.

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The Miscibility of Water and Non-polar Substances at High Temperatures

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Data on the phase equilibria in water-non-polar substance systems at high temperatures and on the relations between the volume, pressure, and composition of the phases involved in these equilibria are considered. The characteristics of the phase equilibria are analysed.
The bibliography includes 66 references.

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I. INTRODUCTION

At normal temperatures the miscibility of water and non-polar substances is very low. With increase of temperature, the miscibility undergoes complex changes and under certain conditions can actually become infinite.

Fairly extensive experimental data have now accumulated on the phase equilibria in water–non-polar substance systems at high temperatures (see the relevant reviews[1-3]). Evidently the available data cannot exhaust the possible wide variety of such mixtures particularly when one takes into account mixtures of several non-polar components with water and mixtures with water containing dissolved salts. It is therefore necessary to formulate general ideas concerning the properties of mixtures of water and non-polar substances which determine the phase equilibria. Such properties are in the first place relations between the chemical potentials (fugacities) of the components and their concentrations, as well as the partial volumes and enthalpies of the components. It is also important to establish to what extent the experimental data obtained are consistent with the existing ideas concerning the molecular nature of the mixtures investigated.

After the description of the phase equilibria in water–non-polar substance systems, this review deals with the characteristics of the variation of the chemical potentials of the components in different phases with pressure, temperature, and composition. In conclusion the phase behaviour in water–non-polar substance systems is explained on the basis of the observed features.

II. GENERAL DESCRIPTION OF THE PHASE EQUILIBRIA IN WATER–NON-POLAR SUBSTANCE SYSTEMS

Two main types of phase behaviour are known for water–non-polar substance systems. The liquid–gas critical curve on the pressure–temperature diagram for the first type consists of two branches. The first branch begins at the critical point of water and either passes through a temperature minimum (Fig. 1*a*) or increases continuously with temperature (Fig. 1*b*) and is directed towards the region of high pressures. This branch probably terminates at very high pressures where the substance solidifies. The second branch begins at the critical point of the non-polar substance and terminates at the critical end point where the critical phase is in equilibrium with some other phase (a second liquid phase, ice, or a clathrate hydrate. For systems of the second type (Fig. 2), the liquid–gas critical curve joins together the critical points of the two components, without splitting into branches. At the same time there exists a liquid–liquid critical curve.

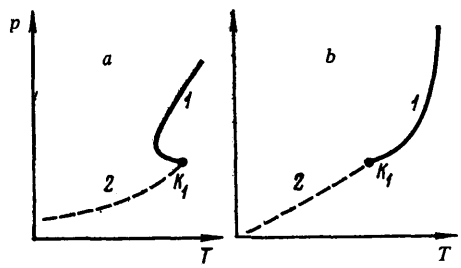


Figure 1. 1) The branch of the critical curve originating at the critical point of water for a water–non-polar substance system (system of type I) (K_1 is the critical point of water); 2) water vapour pressure curve.

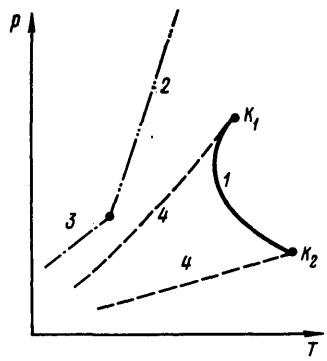


Figure 2. Critical curves for the water–naphthalene system (system of type II) (K_1 and K_2 are the critical points of water and naphthalene respectively): 1) and 2) liquid–gas and liquid–liquid critical curves; 3) liquid–liquid–gas three-phase curve; 4) vapour pressure of the pure substance.

The majority of the water–non-polar substance systems investigated belong to the first type. If the treatment is confined to systems for which the second branch of the critical curve is observed at temperatures where the formation of ice or clathrate hydrates is ruled out, then the pressure–composition diagrams shown in Figs.3–6 are characteristic of equilibria of this type. In Fig.3, which corresponds to a comparatively low temperature, *A* is the region of equilibrium between the solution in the non-polar liquid (henceforth the non-polar or specifically the hydrocarbon liquid) and gas and *B* is the region of equilibrium between the solution of the non-polar substance in water (henceforth the aqueous liquid) and gas. With increase of temperature, there is an increase in the vapour pressures of water and the non-polar substance, of the solubility of water in the non-polar liquid, and of the three-phase equilibrium pressure, and the properties of the non-polar liquid and the gaseous phase involved in the three-phase equilibrium become more similar. This increase in the similarity of the properties terminates with the establishment of the critical state.

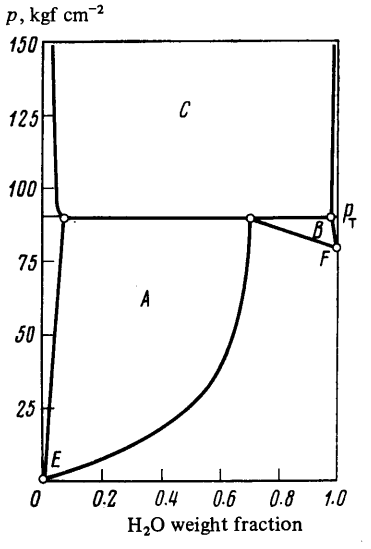


Figure 3. The pressure–composition diagram for a water–non-polar substance system at a temperature below that of the critical end point; *A*, *B*, and *C*—the regions corresponding to non-polar liquid–gas, aqueous liquid–gas, and liquid–liquid equilibria; *E*—vapour pressure of non-polar liquid; *F*—vapour pressure of water; P_T—liquid–liquid–gas three-phase equilibrium pressure.

Fig.4 presents the phase diagram for the same system as in Fig.3 but at a higher temperature, where the properties of the hydrocarbon liquid are the same as those of the gas phase and a critical point *K* appears in the region of the three-phase equilibrium. Since the substance at the critical point is in a region of three-phase equilibrium, it is involved in a phase equilibrium with the aqueous liquid. In this case the critical point is referred to as the critical end point. The equilibrium regions *A* and *B* are in contact at the critical end point.

Fig.5 presents the same system at a temperature exceeding that of the critical end point. At this temperature the three-phase equilibrium no longer exists and regions *A* and *B* are no longer in contact with one another and the critical point *K* is not in equilibrium with the aqueous liquid.

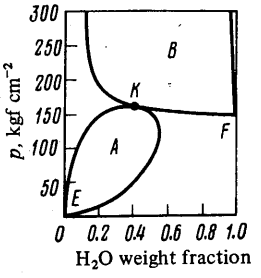


Figure 4. The pressure–composition diagram for a water–non-polar substance system at the temperature of the critical end point (*K* is the critical end point); for the significance of the remaining symbols, see Fig.3.

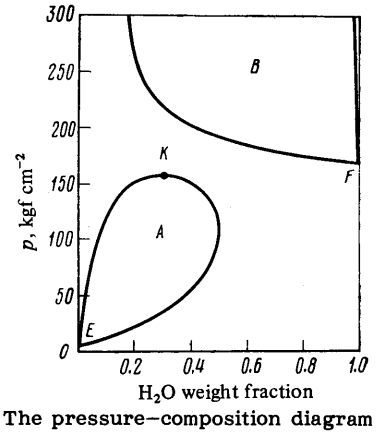


Figure 5. The pressure–composition diagram for a water–non-polar substance system at a temperature above that of the critical end point; for the significance of the symbols, see Figs.3 and 4.

Starting with the temperature of the critical end point and over a certain temperature range above it, region *B* extends up to high pressures without the establishment of the critical state. The establishment of the critical state in region *B* is observed only after the attainment of an extremely high temperature. This is evident from the location of the branch of the critical curve beginning at the critical point of water (Fig.1). For all the water–non-polar substance systems, this branch is bounded by temperatures which are comparatively close to the critical temperature of water. In terms of its nature, the critical curves are of two types in the given case (Figs.1*a* and 1*b*). The commonest type of the critical curve is illustrated in Fig.1*a*. In this case the critical curve is directed from the critical point of water towards low temperatures, reaches a minimum critical temperature, and then rises sharply towards high pressures as the temperature increases. The curve of the second type (Fig.1*b*) is directed from the critical point of water towards high temperatures with a sharp increase of pressure.

Below the minimum critical temperature on the curve illustrated in Fig. 1*a*, critical phenomena are not observed between the gas and the aqueous liquid. At higher temperatures (but not above the critical temperature of water) the constant temperature straight line intersects twice the critical curve and two critical points, characterised by different pressures and compositions, correspond to each temperature T_1 and T_2. The phase diagram in Fig. 6 illustrates precisely this case. The critical points at lower pressures belong to the region of the aqueous liquid–gas phase equilibrium, while those at high pressures belong to the special region of phase equilibria observed when mixtures split up into two layers[4,5] and referred to sometimes as the gas–gas equilibrium. The $p-T$ diagram for systems whose $p-N$ diagrams are illustrated in Figs. 3–6 is presented in Fig. 7. For the system whose critical curve is shown in Fig. 1*b*, the pressure–composition phase diagram has the form illustrated in Fig. 8.

A considerable number of binary systems showing the above type of phase behaviour have now been investigated at high temperatures. Table 1 presents certain characteristics of such systems. Almost all the systems investigated are binary. The phase equilibria in the nitrogen–hexadecane–water ternary systems have been studied[28,29]. The naphthalene–water[21], tetrahydronaphthalene–water[30], and decahydronaphthalene–water[30] systems exhibit the second type of phase behaviour of hydrocarbon–water systems.

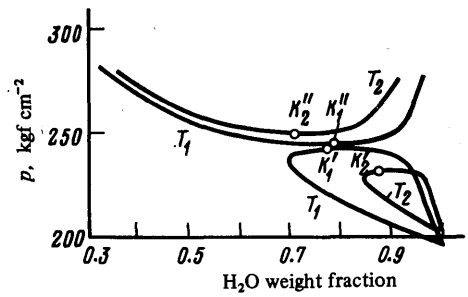


Figure 6. The pressure–composition diagram for a water–non-polar substance system in the vicinity of the critical point of water; K'_1 and K'_2—critical points for the liquid–gas equilibrium; K''_1 and K''_2—critical points for the gas–gas equilibrium.

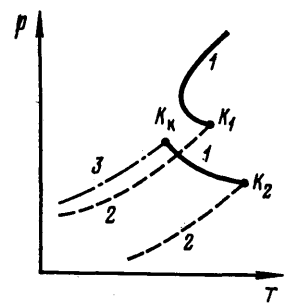


Figure 7. The pressure–temperature diagram for a water–non-polar substance system; K_1 and K_2—critical points of water and the non-polar substance: 1) critical curve; 2) vapour pressure of pure substance; 3) three-phase curve; K_t—critical end point.

Table 1. Characteristics of binary water–non-polar substance systems.

Non-polar component	Critical end point			Refs.	Minimum critical temperature			Refs.
	t, °C	p_λ, kgf cm^{-2}	H_2O, mole fraction		°C	p, kgf cm^{-2}	H_2O, mole fraction	
Methane	*	—	—	—	351.9	965	0.825	6,7
Ethane	*	—	—	—	350	716	0.78	8
Propane	96.5	43.3	0.0099	9	—	—	—	—
Propane	96.7	42.7	—	10	—	—	—	—
n-Butane	152.0	43.4	0.0483	11	351.0	374	0.89	8
n-Butane	150.0	41.6	—	10	**			12
n-Pentane	190.6	44.8	—	10	351.0	340	0.595	13
n-Hexane	222.0	52.1	0.322	14	349.5	312	0.881	15
n-Hexane	225.0	52.3	—	10	—	—	—	—
n-Hexane	225.1	54.4	0.260	16, 17	—	—	—	—
n-Heptane	245.4	67.9	0.370	16, 17	353	290	0.651	13
n-Heptane	246.1	64.4	—	10	—	—	—	—
n-Octane	267.2	73.1	—	10	351.5	281	0.906	15
n-Octane	267.2	76.7	0.490	16, 17	—	—	—	—
n-Nonane	280.0	90.0	0.575	16, 17	—	—	—	—
n-Nonane	282.2	87.2	—	10	—	—	—	—
n-Decane	296.1	98.1	—	10	353.0	258	0.923	15
n-Decane	296.0	99.7	0.680	16, 17	—	—	—	—
n-Dodecane	314.0	133	0.770	16, 17	342.0	205	0.948	15
n-Hexadecane	338.0	160	0.900	18	362.0	244	0.976	18
n-Eicosane	352.0	185	0.923	16, 17	—	—	—	—
Benzene	287.8	95.7	—	19	294.0	216	0.777	20
Benzene	288.3	92.8	0.602	20	294.0	216	0.780	21
Benzene	289.4	96.5	—	10	—	—	—	—
Toluene	285.0	102.9	—	10	—	—	—	—
Ethylbenzene	301.1	114.2	—	10	—	—	—	—
Cyclohexane	255.6	81.8	0.493	22	341	300	0.8	15
	256.7	82.0	—	10	—	—	—	—
Methylcyclohexane	271.1	84.9	—	10	—	—	—	—
Propene	—	—	—	—	**	—	—	23
Argon	—	—	—	—	350	—	—	25
Argon	—	—	—	—	—	—	—	24
Xenon	—	—	—	—	344	700	0.640	26
Nitrogen	—	—	—	—	364	760	0.820	27

*Does not exist.

**Gas–gas equilibrium of the first type.

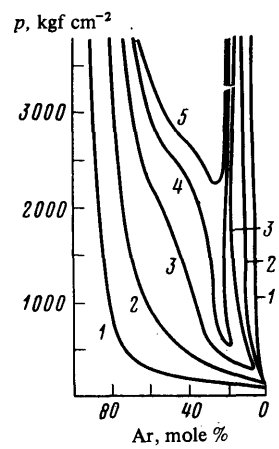


Figure 8. The pressure–composition diagram for a water–non-polar substance system (for a system with the critical curve illustrated in Fig. 1*b*) in the vicinity of the critical point of water at different temperatures (°C): 1) 300; 2) 350; 3) 375; 4) 385; 5) 390.

III. GASEOUS MIXTURES OF WATER AND NON-POLAR SUBSTANCES

The fugacities, partial volumes, and partial enthalpies of the components of the gaseous mixture can be found from the relation between the volume, pressure, temperature, and mixture composition ($p-V-T-N$ data). Such data are available for a number of binary gaseous mixtures of water vapour and non-polar substances. Table 2 lists the mixtures investigated and gives the temperatures and pressure ranges where the relevant experimental determinations were made over a wide range of compositions.

Table 2. The temperature and pressure ranges in which the volumes of gaseous mixtures of water and non-polar substances were investigated.

t, °C	p, kgf cm^{-2}	t, °C	p, kgf cm^{-2}
Methane (Refs.31,32)		Nitrogen (Refs.31,32)	
250	65	250	50
300	85	300	80
350	150	390	600
380	600	Xenon (Ref.26)	
n-Hexane (Ref.33)		375	3000
250	42	400	3000
300	85	450	3000
350	150	500	3000
n-Octane (Ref.33)		Argon (Ref.24)	
350	100	450	3000
n-Decane (Ref.34)			
275	60		

The volumes of the gaseous mixtures of water vapour with hydrocarbons and nitrogen below the critical temperature of water and at pressures which do not exceed greatly the water vapour pressure are reproduced satisfactorily with the aid of the Redlich–Kwong equation of state modified by Prausnitz and coworkers[35] for mixtures of water and non-polar components. This equation is apparently suitable for the description of the volumes of gaseous mixtures of non-polar components with water vapour also above the critical temperature of water, provided that the pressure does not exceed 200–250 kgf cm^{-2}.

The Redlich–Kwong equation is

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)\,T^{0,5}} . \qquad (1)$$

The coefficient of Eqn.(1) for a mixture is usually expressed in terms of the coefficients of the mixture components and their mole fractions with the aid of the equations

$$b = \sum_i b_i N_i, \; a = \sum_i \sum_j a_{ij} N_i N_j, \qquad (2)$$

$$b_i = 0{,}0867 RT_{K_i}/P_{K_i}, \; a_{ii} = 0.4278\; R^2 T_{K_i}^{2,5}/P_{K_i}, \qquad (3)$$

$$a_{ij} = a_{ii}^{0,5} a_{jj}^{0,5},$$

where p is the pressure, v the molar volume, N the mole fraction, R the gas constant, and T the absolute temperature.

Eqns.(2) and (3) are relatively unsuitable for both water and for water–non-polar substance mixtures. Two modifications have been introduced[35] into Eqns.(3). Firstly, account was taken of the fact that the coefficient a for water is not constant but decreases appreciably with temperature. This is because the interaction between water molecules is to a large extent determined by hydrogen bonds and dipole–dipole interactions. The above interactions are extremely sensitive to the mutual orientation of water molecules and therefore diminish sharply with increased temperature. The coefficients a_{11} for water (henceforth water will be designated by subscript 1 and the non-polar substance by 2) at different temperatures have been determined from data for the dependence of the volume of water vapour on pressure; the corresponding values of a_{11} have been tabulated as a function of temperature[35].

The necessity for the second modification in Eqn.(3) arises from the fact that, when water molecules interact with non-polar molecules, neither hydrogen bonds nor dipole–dipole interactions, which play the main role in the interaction of water molecules with one another, occur. The coefficient a_{11} was divided into two parts:

$$a_{11}(T) = a_{11}' + a_{11}''(T). \qquad (4)$$

The quantity a_{11}' is independent of temperature and is determined by dispersion interaction forces, while a_{11}'' is determined by hydrogen bonds and dipole–dipole interactions. In the calculation of the mixed coefficient a_{1j} for water and the non-polar substance from the last Eqn.(3), account is not taken of the entire coefficient a_{11} but only of that part of it which contributes to the water–non-polar substance interaction (a_{11}')†:

$$a_{1j} = (a_{11}' a_{jj})^{0,5}. \qquad (5)$$

According to Prausnitz and coworkers[35], $a_{11}' = 35$ kg K$^{1/2}$ litre^2 mol^{-2}.

The unsuitability of the method of Prausnitz and coworkers[35] for the description of $p-V-T-N$ data for mixtures in which water vapour predominates at temperatures above the critical temperature of water and at pressures in excess of 200 kg cm^{-2} is due to the fact that the coefficient a_{11} of the Redlich–Kwong equation for pure water vapour begins to depend appreciably on pressure when the latter is above 200–300 kg cm^{-2}.

The Redlich–Kwong equation with the modifications described has been tested not only for the volumes of gaseous mixtures but also in relation to the phase equilibria. The equation

$$\ln f_i = \ln \frac{N_i RT}{v-b} + \frac{b_i}{V-b} - \frac{2\sum_j N_j a_{ij}}{RT^{3/2} b} \ln \frac{v+b}{v} + \frac{ab_i}{RT^{3/2} b^2}\left[\ln \frac{v+b}{v} - \frac{b}{v+b}\right] \qquad (6)$$

with the aid of which the chemical potential (fugacity) of the mixture component f_i is determined, corresponds to the equation of state (1). Eqn.(6) was tested with the aid of data for phase equilibria between water and gas. Since the solubility of non-polar substances in water is as a rule very low, the fugacity of water in the aqueous liquid can be set equal to the tabulated fugacity of pure water multiplied by the mole fraction of water in the liquid, which is close to unity, and by Poynting's correction, which takes into account the amount by which the pressure exceeds the water vapour pressure. Having substituted this value in Eqn.(6), we find from Eqns.(6) and (1) the concentration of water vapour in the gas saturated with water at the given pressure.

†An analogous approach has been proposed by M.I.Temkin[36].

Table 3[37] presents systems for which calculation of the water vapour content in the gas in equilibrium with water proved to be satisfactory over a specific range of temperatures and pressures.

Table 3. Errors in the calculation of the water vapour content of the gas in equilibrium with water (average for several pressures).

t, °C	P_{max}, kgf cm^{-2}	Error, %	t, °C	P_{max}, kgf cm^{-2}	Error, %
	Methane			n-Hexane	
150	400	2.7	200	37	1.8
200	400	3.6	220	53	2.2
250	400	3.4	235	150	3.1
300	400	2.8	250	150	3.7
			275	150	4.5
	n-Butane			n-Decane	
171.1	562	2.4	300	100	8.9
204.4	562	2.3	310	100	9.2
237.8	421	2.9			

Attention should be drawn to the fact that in many instances calculation of the water vapour content in a non-polar gas by Eqns.(1) and (6) leads to satisfactory results also at those temperatures and pressures at which Eqn.(1) is unsuitable for the calculation of the volume of pure water vapour. The cause of this discrepancy lies in the fact that the region of applicability of Eqn.(1) to non-polar gases is wider than the region of its applicability to water vapour. When the content of water vapour in the gaseous mixture is low, Eqn.(1) describes the volumes of the mixture at pressures where it is unsuitable for mixtures with a high content of water vapour.

The applicability (within certain regions of the parameters of state) of the equation of state to gaseous mixtures of water vapour and non-polar components makes it possible to calculate the chemical potentials of the components of the above systems and their dependence on pressure and composition, i.e. all the data required for calculations on phase equilibria. The majority of the calculations based on the equation of state are carried out on a computer; the calculations can yield information about the behaviour of specific systems. However, general analysis of the behaviour of systems as a function of the properties of a non-polar substance with the aid of a computer is difficult. The approximate method for estimating the volume behaviour of mixtures described below is therefore of interest. The volumes of mixtures are frequently described by means of a quantity called the excess volume:

$$v_{exc} = v - v_1^0 N_1 - v_2^0 N_2, \qquad (7)$$

where v_1^0 and v_2^0 are the molar volumes of the pure components and v is the molar volume of the mixture.

Figs.9 and 10 present the excess volumes in the water–methane[31,32] and water–octane[33] systems. At low and moderate pressures the excess volume is positive in all the systems investigated; in individual instances the volume exceeds by 20–30% the additive volume of the components. With increase of pressure, the excess volume behaves in a fairly complex manner in many instances. Thus in the water–octane system (Fig.10) mixtures in which water predominates are characterised, as before, by the increase of the volume above the additive value, while mixtures in which the hydrocarbon predominates have a volume smaller than the additive value, i.e. the excess volume curve has a maximum and a minimum. On further increase of pressure, the excess volume becomes negative over the entire range of compositions.

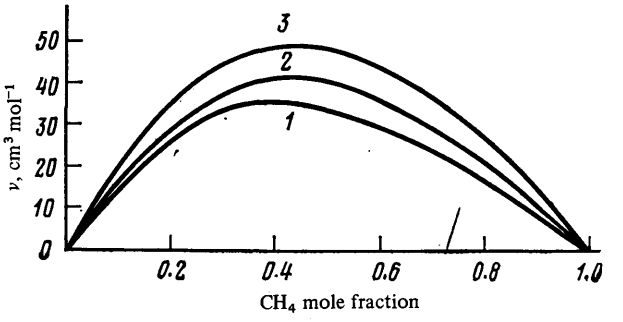


Figure 9. The excess molar volumes in the methane–water system at 350 °C and at different pressures (kgf cm^{-2}): 1) 60; 2) 100; 3) 140.

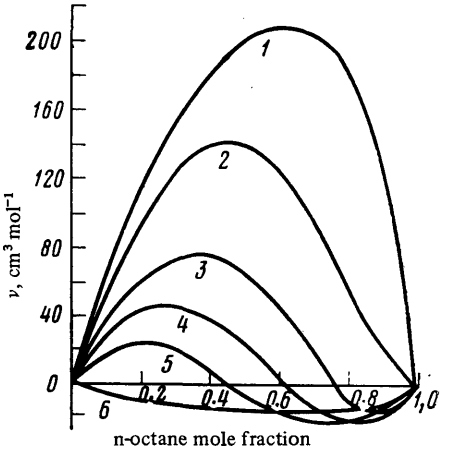


Figure 10. The excess molar volumes in the octane–water system at 350 °C and at different pressures (kgf cm^{-2}): 1) 40; 2) 60; 3) 80; 4) 100; 5) 120; 6) 140.

Calculations of the volumes by the Redlich–Kwong equation with Prausnitz's modifications reproduce the different forms of dependence on the excess volume and composition presented in Fig.10. On the assumption that this equation is applicable to the description of excess volumes in gaseous

solutions, it is possible to carry out a general analysis of the volume behaviour of the test systems as a function of the nature of the non-polar substance, which is determined by the coefficients a_{22} and b_2.

Since the equation of state (1) has been solved for pressure, analysis is greatly simplified when the excess pressure is used instead of the excess volume. The excess pressure is the difference between the true pressure of the mixture and the pressure calculated from Dalton's law, i.e. obtained by adding together the pressures of the pure components (p_1^0 and p_2^0) of the mixture occupying the same volume as the mixture:

$$p_{exc} = p - p_1^0 N_1 - p_2^0 N_2. \quad (8)$$

Since the behaviour of the excess pressure and excess volume is qualitatively similar, for an approximate estimate of the behaviour of the excess volume one can employ data for the behaviour of the excess pressure.

The form of the dependence of the excess pressure on composition is determined primarily by the sign of the derivatives $\partial p_{exc}/\partial N_1$ at the ends of the composition axis, i.e. at $N_1 = 0$ and $N_1 = 1$. For the excess pressure maximum, it is necessary that

$$(\partial p_{exc}/\partial N_1)_{v,T,N_1=0} > 0 \text{ and } (\partial p_{exc}/\partial N_1)_{v,T,N_1=1} < 0. \quad (9)$$

For the simultaneous presence of an excess pressure minimum in mixtures with a high content of the non-polar substance and an excess pressure maximum in mixtures with a high water vapour content, it is necessary that

$$(\partial p_{exc}/\partial N_1)_{v,T,N_1=0} < 0 \text{ and } (\partial p_{exc}/\partial N_1)_{v,T,N_1=1} < 0. \quad (10)$$

Finally, for an excess pressure minimum, it is necessary that

$$(\partial p_{exc}/\partial N_1)_{v,T,N_1=0} < 0 \text{ and } (\partial p_{exc}/\partial N_1)_{v,T,N_1} > 0. \quad (11)$$

The van der Waals equation

$$p = RT/(v-b) - a/v^2 \quad (12)$$

can be used for the approximate analysis of the above problem instead of the Redlich–Kwong equation (1). Eqn.(12) differs little from Eqn.(1) at constant temperature and at not unduly high pressures. It is noteworthy that, despite the identical designation of the coefficients of Eqns.(1) and (12), their numerical values are different. Using Eqns.(12), (2), and (5), it is possible to obtain the expressions

$$(\partial P_{exc}/\partial N_1)_{v,T,N_1=0} = \frac{RT(b_1-b_2)}{(v-b_2)^2} - \frac{RT}{v-b_1} + \frac{RT}{v-b_2} + \frac{a_{11}+a_{22}-2a_{12}}{v^2}, \quad (13)$$

$$(\partial P_{exc}/\partial N_1)_{v,T,N_1=1} = \frac{RT(b_1-b_2)}{(v-b_1)^2} - \frac{RT}{v-b_1} + \frac{RT}{v-b_2} + \frac{2a_{12}-a_{11}-a_{22}}{v^2}. \quad (14)$$

For higher values of v (i.e. at low pressures), the sum of the first three terms of Eqns.(13) and (14) can be neglected compared with the fourth term. Since $a_{12} < (a_{11}+a_{22})/2$ conditions (9) hold at low pressures. With increase of v, the first terms of Eqns.(13) and (14) begin to increase in absolute magnitude; their sign is negative for $b_2 > b_1$. The first term of Eqn.(13) then increases faster than the first term of Eqn.(14), so that, on passing to small volumes (i.e. high pressures), the derivative $(\partial p_{exc}/\partial N_1)_{v,T,N_1=0}$ can change sign before $(\partial p_{exc}/\partial N_1)_{v,T,N_1=1}$ and two extrema are observed [condition (10)]; finally, on further increase of pressure, the derivative $(\partial p_{exc}/\partial N_1)_{v,T,N_1=1}$ also changes sign and an excess pressure minimum is observed [condition (11)].

Thus, subject to the condition that the volume of the molecule of the non-polar substance exceeds that of the water molecule ($b_2 > b_1$), conditions (9), (10), and (11) should be established successively with increase of pressure. The greater the volume of the molecule of the non-polar substance, the higher the pressure at which the above changes in the excess volume (pressure) occur. One should recall that the behaviour described is observed only in the region of applicability of the equation of state adopted.

It is noteworthy that the principal specific feature of gaseous solutions of water and a non-polar substance is an extremely weak interaction between unlike molecules. This feature is manifested both at low and at high temperatures. The structural order characteristic of the liquid phase is not significant in gaseous solutions at low densities. The inapplicability of simple two-parameter equations of state to high-density water vapour should apparently be attributed to this factor.

IV. LIQUID SOLUTIONS OF NON-POLAR SUBSTANCES IN WATER

There are very few data for solutions of non-polar substances in water which could yield information about the thermodynamic quantities of the solutions over a wide range of temperatures and pressures. The solutions of methane in water have been most thoroughly investigated. Data for the solubility of methane in water and the volumes of the solutions at low and moderate temperatures have been available for a comparatively long time[38,39] and those for the range 200–350 °C were obtained more recently[7,40,41].

The Henry coefficient H_i can be found from solubility data. By definition[42], it is related to the difference between the chemical potential of component i at infinite dilution, extrapolated to the pure substance, and the chemical potential of the component in the ideal gas state at $p = 1$:

$$RT \ln H_i = \mu_i(p, T) - \mu_i(\text{id.gas}, T, p=1). \quad (15)$$

Here H_i is the Henry coefficient, μ_i is the chemical potential of component i, and the dot under the symbol means that the given quantity refers to the state of infinite dilution. Knowing the dependence of the Henry coefficient on temperature, it is possible to obtain by means of Eqn.(15), with the aid of a familiar thermodynamic relation, the enthalpy change for transfer of component i from the ideal gas state to an infinitely dilute solution:

$$\left(\frac{\partial \ln H_i}{\partial T}\right)_p = -\frac{(h_i - h_{i,\text{id.gas}})}{RT^2}, \quad (16)$$

where h_i is the partial molar enthalpy of component i.

The solutions of methane as well as the majority of other non-polar substances in water are characterised by two features at low temperatures: firstly, on formation of these solutions from an ideal gas and water, the enthalpy decreases (heat is evolved) and, secondly, the Henry coefficient of the non-polar substance dissolved in water is very high (and correspondingly the solubility is extremely low).

The characteristics of the solubility of non-polar substances in water at low temperatures are said to be related to the ideas concerning the structure of liquid water. It is known that at low temperatures liquid water to a large extent retains the structure of ice within the limits of short-range order. In the structure of ice water molecules are distributed relative to one another in such a way that each is involved in the maximum possible number of hydrogen bonds (four bonds). By virtue of the high energy of the hydrogen

bonds, ice is fairly stable despite the small coordination number; the small coordination number is responsible for the extremely loose packing characterised by the presence of comparatively large cavities. In liquid water at low temperatures some of the cavities are filled by water molecules[43], which are linked to the molecules surrounding the cavities by dispersion interaction forces.

Apparently at low temperatures the non-polar molecules incorporated in water disrupt the hydrogen bonds existing between water molecules to only a slight extent, but they transform the water structure around themselves in such a way that cavities arise in the latter in which the non-polar molecules can be accommodated. The evolution of heat (decrease of enthalpy) on formation of a liquid solution from a non-polar substance in the ideal gas state and water is then related to the absence of a significant energy expenditure on the dissociation of hydrogen bonds and to the gain of the dispersion interaction energy by the molecules of the non-polar substance. A certain amount of energy is also evolved because the water molecules displaced by the non-polar substance from the cavities form hydrogen bonds with one another[44-46].

The second feature of solutions of non-polar substances in water at low temperatures, namely their low solubility, has not yet received a generally accepted explanation[46,47]. Attempts to explain the low solubility of non-polar substances in water have been made in two investigations[48,49]. It has been suggested[49] that the formation of cavities in water, whose volume makes it possible to accommodate non-polar molecules larger than helium and neon atoms and hydrogen molecules#, is not accompanied by a change in enthalpy, but proceeds with a decrease of entropy. The decrease of entropy is associated with the increase of the Henry coefficient in accordance with the thermodynamic equation

$$RT \ln H_i = \Delta h_i - T\Delta S_i; \qquad (17)$$

where Δh_i and ΔS_i are the change in the enthalpy and entropy on transfer of the non-polar substance from the ideal gas state at $p = 1$ to the hypothetical state of the solute extrapolated to the pure substance.

At high temperatures (starting from ~100 °C) the solubility of methane in water increases with temperature at an increasing rate[41]. According to Eqn.(16), this corresponds to a negative heat of solution, i.e. to the absorption of heat. This finding is consistent with data showing that, under the conditions of intense thermal movement, ordered structures in water lose their importance. In the limit at a sufficiently high temperature both water and methane molecules in solutions are distributed completely at random and water–water interactions are replaced by water–methane interactions in the dissolution process. As already mentioned, this change should take place with loss of energy. The internal energy for the intermolecular interaction of the ideal gas is zero. Thus at high temperatures the change in the internal polar energy on dissolution will be greater than zero ($e_i - e_{i,\text{id.gas}} > 0$). The work associated with the decrease of the volume of the gas when the latter dissolves is also positive; consequently the entropy change is likewise positive ($h = e + pv$).

The difference in the nature of the solubility of non-polar substances in water at low and high temperatures is also indicated by the partial molar volume of the substance dissolved in water. For example, the partial molar volumes of methane dissolved in water at 0° and 50 °C [40] are much smaller than the corresponding quantities for the methane dissolved in other solvents[48].

Partial molar volumes of methane dissolved in water at 400 kgf cm^{-2} and different temperatures

t, °C	0	50	100	150	200	250	300	350
v, /cm^3	36	38	40	43	49	60	96	141

It is seen from the data presented that, starting from 250 °C and at higher temperatures (300° and 350 °C), the partial molar volume of methane dissolved in water increases sharply. This finding is consistent with the idea that at high temperatures the water–water interaction is replaced by the water–methane interaction on dissolution of methane, which should be accompanied by a considerable decrease of the forces of interaction between molecules.

A sharp difference between the mechanisms of the dissolution of methane in water is apparently observed at markedly different temperatures. For intermediate temperatures, there is probably a possibility of a mixed dissolution mechanism in which methane molecules are both incorporated in cavities and replace water molecules in the quasi-crystal lattice of the liquid (the "cavity" and "solvation" mechanisms according to Borina and Samoilov[52]).

Using data for the solubility of methane in water, the equations of state for the gas phase (the Lewis–Randall rule at low concentrations of water vapour and the Redlich–Kwong equation at high concentrations), and data for the change in the volume of water on dissolution of methane in the latter, it is possible to determine the changes in the fugacity of methane as a function of its concentration in solution. It has been established for the range 25–171 °C that a solution of methane in water at pressures up to 700 kgf cm^{-2} obeys Henry's law in terms of the thermodynamic formulation[53]:

$$f_2 = H_2(p, T)N_2, \qquad (18)$$

$$H_2(p,T) = H_2(p_1^0, T) \cdot 10^{\frac{v_2(p-p_1^0)}{2.303\,RT}}; \qquad (19)$$

here subscripts 2 and 1 correspond to methane and water respectively. When Eqn.(18) holds and v_2 is independent of pressure, there should be a linear relation between $\lg(f_2/N_2)$ and $p - p_1^0$.

Between 300° and 350 °C, the linear relation between $\lg(f_2/N_2)$ and $p - p_1^0$ does not hold, which can be attributed both to a decrease of the partial molar volume of methane with pressure at high temperatures and to the failure of the Henry law (or to both causes simultaneously). When Henry's law breaks down, an additional multiplier is introduced into Eqn.(18)—the activity coefficient γ, which determines the degree of deviation from Henry's law:

$$f_2 = H_2(p,T)N_2\gamma_2^\infty, \qquad (20)$$

where ∞ refers to infinite dilution. The activity coefficient γ_2^∞ is close to unity in the region of low methane concentrations, but apparently diminishes as the concentration increases. The hypothesis of the decrease of the activity coefficient with concentration is associated with the fact that, at temperatures exceeding the minimum critical temperature in the water–methane system (352 °C), the critical state can be reached; at the critical point of the mixture the fugacity of the component does not vary with concentration:

$$(\partial \ln f_i/\partial N_i)_{p,T} = 0. \qquad (21)$$

#Molecules whose size exceeds these dimensions cannot be accommodated within the cavities of the ice lattice[50,51].

Fig.11 illustrates the variation of the fugacity with the mole fraction when Henry's law holds (dashed line) and the variation of the fugacity in the vicinity of the critical point associated with condition (21), which is obligatory for the critical point of a binary system. It is seen from Fig.11 that, as the critical is approached, the fugacity deviates from the value which it should have when the Henry law holds. This means that the activity coefficient should become less than unity.

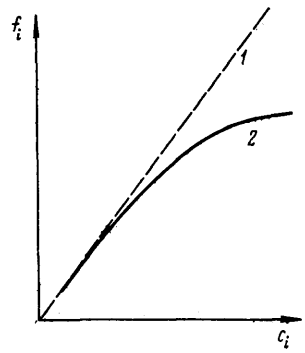


Figure 11. Variation of the fugacity of the component in solution with its concentration: 1) Henry's law; 2) real relation.

The problem of the variation of the properties of a solution of a non-polar substance in water under the influence of the addition of a salt to water is extremely interesting. Bearing in mind that the solubility of non-polar substances in water is extremely low, in most cases it is possible to assume that the chemical potential of water in the aqueous salt solution of a non-polar substance is the same as in the aqueous salt solution without the non-polar substance. The corresponding chemical potentials of water can be found from its vapour pressure over the salt solution. If necessary, a correction is introduced for the difference between the vapour pressure and fugacity and a correction for the Poynting effect when the external pressure exceeds the vapour pressure.

The influence of the salt dissolved in water on the chemical potential of the non-polar solute is much more complex. The solubility of non-polar substances in water in most cases decreases under the influence of salts. The change in solubility is usually described with the aid of Sechenov's equation

$$N_i^* = N_i \cdot 10^{-K_i n}, \qquad (22)$$

where the superscript * refers to the electrolyte solution.

Eqn.(22) holds fairly accurately only at low salt concentrations. At salt concentrations in excess of 0.5–1 M the Sechenov coefficient K_i usually decreases with increase of concentration.

An expression for the Henry coefficient of the non-polar component dissolved in a salt solution in water can be obtained from Eqn.(22) and the definition of the Henry coefficient:

$$H_i^* = H_i \cdot 10^{K_i n}.$$

It is usually assumed that the limits of the applicability of the Henry law [Eqns.(18) and (19)] to non-polar gases dissolved in aqueous salt solutions do not differ significantly from the limits of the applicability of this law to solutions of gases in water without salts.

The temperature dependence of the Sechenov coefficient has been investigated mainly in the range 0–70 °C. At high temperatures the influence of salts on the solubility of non-polar gases has been studied only for carbon dioxide[54,55] and methane[56] and it has been found that the Sechenov coefficient passes through a minimum as a function of temperature. To account for this phenomenon, one must relate the Sechenov coefficient to the thermodynamic functions of component i disssolved in water[57].

Consider the equilibrium between component i in the gas state and both pure water and a salt solution of water in the region where Henry's law holds:

$$\mu_i(\text{gas}) = \mu_i + RT \ln N_i = \mu_i^* + RT \ln N_i^*. \qquad (23)$$

It follows from Eqns.(22) and (23) that

$$\mu_i^* - \mu_i = 2.303\, RT\, n K_i. \qquad (24)$$

According to Eqn.(24), the Sechenov coefficient is related to the difference between the chemical potential of component i in pure water and in the salt solution. Differentiation of Eqn.(24) with respect to temperature yields

$$\frac{h_i - h_i^*}{RT^2} = 2.303\, n \frac{\partial K_i}{\partial T}, \qquad (25)$$

The minimum in the plot of the Sechenov coefficient against temperature is apparently associated with the different natures of solutions of non-polar substances in water at low and high temeratures. If the non-polar molecules in solution in water at low temperatures are located in cavities, then, according to Eqn.(25), the temperature variation of the Sechenov coefficient is determined by the difference between the internal energies of the non-polar substance in pure water and in the salt solution. The internal energy of the intermolecular interaction between the non-polar substance and the skeleton of the water lattice is relatively small and the change in this interaction under the influence of the salt is even smaller.

At a high temperature[57] the formation of the solution involves mainly the replacement of water molecules by those of the non-polar gas in the quasi-crystal lattice. The enthalpy of formation of the solution from the non-polar gas in the ideal gas state and from liquid water can then be regarded as consisting of two components: the main, positive part—the enthalpy of the separation of water molecules from one another on formation of a cavity for the incorporation of the non-polar molecules (e_1)—and a small negative part—the enthalpy of incorporation of non-polar molecules at a quasi-crystal lattice site of water (e_{inc}).

Neglecting the enthalpy of the incorporation of the non-polar substance compared with the enthalpy of formation of a cavity in the water lattice, we find that, for a small difference between the sizes of water molecules and the molecules of the non-polar substance,

$$\left(\frac{\partial K_i}{\partial T}\right)_p \approx \frac{h_1 - h_1^*}{2.3 n RT^2}; \qquad (26)$$

where n is the molality of the electrolyte in solution. It can be shown that

$$\frac{h_1 - h_1^*}{2.3 \cdot RT^2 n} = \left(\frac{\partial \lg (f_1^*/f_1^0)}{\partial T}\right), \qquad (27)$$

where f_1^0 and f_1^* are the fugacities of pure water and the water in the salt solution.

Calculations based on the experimental water vapour pressures over salt solutions[58] show that $h_1 - h_1^* > 0$ and increases with temperature. It follows from this finding that, in conformity with Eqn.(26), the Sechenov coefficient should increase with temperature at high temperatures. The available data for the variation of the Sechenov coefficients confirm Eqn.(26) approximately[54-56] (Fig.12).

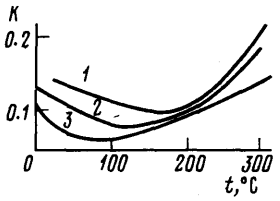


Figure 12. Temperature dependence of the Sechenov coefficients K of gases dissolved in aqueous salt solutions: 1) methane in NaCl solution; 2) carbon dioxide in $CaCl_2$ solution; 3) carbon dioxide in NaCl solution.

On the whole, one should note that the nature of solutions of non-polar substances in water at low temperatures is determined by the distribution of the molecules of the non-polar substance in the structural cavities. At high temperatures the specific features of the dissolution process involve the substitution of water molecules by solute molecules. The changes in the nature of the dissolution process with temperature lead to minima in the temperature variations of the Henry and Sechenov coefficients of non-polar substances dissolved in water.

V. LIQUID SOLUTIONS OF WATER IN NON-POLAR SUBSTANCES

It was noted above that water as a solvent for non-polar substances differs sharply from other solvents: the Henry coefficients of non-polar substances dissolved in it exceed by 2–3 orders of magnitude (and more) their values for the same substances in the majority of other solvents§. Water as a solute in non-polar solvents is not exceptional among other solutes. This is because the specific features of water are manifested in the interaction of its molecules with one another—mainly in the formation of hydrogen bonds. On the other hand, the separated molecules of the water dissolved in a non-polar solvent do not exhibit features characteristic of a collection of water molecules. If the properties of water in its dilute liquid solutions in non-electrolytes are extrapolated to the hypothetical pure substance, then the latter should have properties close to those of non-polar substances with small molecules—for example, methane or nitrogen, i.e. substances whose critical temperature is lower by hundreds of degrees than that of water.

Henry coefficients (kgf cm^2) of water and methane in different solvents (Refs.59-62)

Solvent	n-Butane	n-Decane	n-Hexadecane
t, °C	37.7	237.8	250
Water	140	150	190
Methane	190	250	200

§Certain aromatic hydrocarbons are an exception.

Evidently the Henry coefficients of water and methane in different non-polar solvents are of the same order of magnitude.

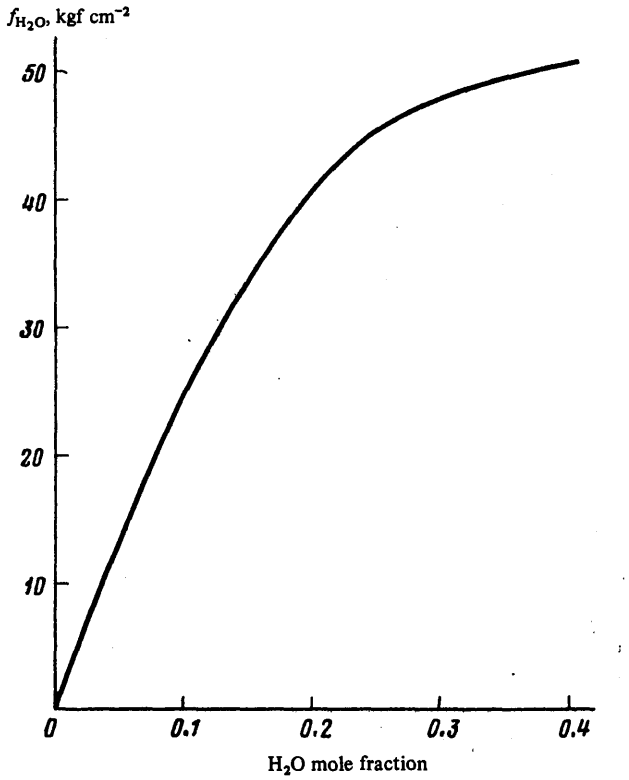


Figure 13. Dependence of the fugacity of water on its concentration in a decane–water mixture at 275 °C and a pressure of 73.2 kgf cm^{-2}.

There are at present numerous data for the phase equilibria between liquid non-polar substances and gaseous mixtures and between liquid non-polar substances and liquid aqueous solutions. Information concerning certain thermodynamic properties of solutions of water in non-polar substances can be obtained from these data. For example, in view of the possibility of calculating the fugacities of the components in gaseous solutions from the equation of state (see Section III), it is possible to find the fugacities of the components in liquid solutions in equilibrium with the gas phase along the saturation line. There are fewer data for the volumes of solutions of water in liquid non-polar substances.

Relatively detailed information is available about both phase equilibria and the volumes for solutions of water in decane at 275 °C.[34] The dependence of the fugacity of water on its mole fraction in its liquid solution at 275 °C and a pressure of 73.2 kgf cm^{-2} has been obtained from these results (Fig.13). Fig.13 shows that, at water concentrations not exceeding a mole fraction of 0.1, a linear relation holds between the fugacity and concentration (thermodynamic formulation of the Henry law) within the limits of experimental accuracy; for mole fractions in excess of 0.1, the increase of fugacity slows down. The activity coefficient γ_1^{∞} in Eqn.(20), corresponding to a mole fraction of 0.4, is appreciably smaller than unity (0.48). The decrease of the activity coefficient is apparently associated with the approach to the critical state [see Eqn.(27)].

The data of Lotter et al.[34] show that at 275 °C and 69.5 kgf cm^{-2} the molar volume of a liquid solution of water in decane varies linearly with concentration when the latter changes from a mole fraction of 0.1 to 0.35. From this it follows that the partial molar volume of water in the above concentration range is constant. Its value under these conditions is 119 cm^3 mol^{-1}, which is much greater than the molar volume of pure water under the same conditions (23.6 cm^3 mol^{-1}).

Measurements of the volumes of solutions of water in various non-polar substances at the same concentration for each hydrocarbon[63] made it possible to calculate the apparent molar volume of dissolved water as the ratio of the volume increment on dissolution of water in the non-polar substance to the number of moles of dissolved water:

$$v_1^{app} = [v - v_2^0(1 - N_1)]/N_1 . \qquad (28)$$

The results (Table 4) exceed severalfold the molar volumes of pure water, which varies from 21.4 to 28.1 cm^3 mol^{-1} under the given conditions.

Table 4. The apparent molar volumes of water v_{eff} dissolved in hydrocarbons.

Hydrocarbon	t, °C	p, kgf cm^{-2}	v_{eff}, cm^3 mol^{-1}	Mole fraction
n-Hexane	220	48	641	0.185
n-Decane	285	67	146	0.319
n-Hexadecane	275	56	86	0.338
	300	81	99	0.428
	330	125	110	0.531

The partial molar volumes of water dissolved in hydrocarbons apparently decrease markedly with increase of pressure. Using data for the phase equilibria in liquid water and decane at 275 °C and pressures up to 800 kgf cm^{-2},[34] neglecting the solubility of decane in water, and assuming (as mentioned above) that the Henry law holds for a water mole fraction in the hydrocarbon less than 0.1, the partial molar volume of water in decane can be found from the differential equation for the phase equilibrium

$$\left(\frac{\partial N_1^n}{\partial p}\right)_T = \frac{v_1^w - \bar{v}_1^n}{RT\,(\partial \ln N_1^n/\partial N_1^n)} \qquad (29)$$

where superscripts n and w refer to the non-polar liquid phase and to the aqueous phase respectively. It was found that, at a pressure of 700 kgf cm^{-2}, it is much smaller than the experimental partial volume of water at 70 kgf cm^{-2}.

VI. CHARACTERISTICS OF THE PHASE EQUILIBRIA IN THE SYSTEMS UNDER CONSIDERATION

The knowledge of the thermodynamic properties of the individual phases in a water–non-polar substance system makes it possible to explain the characteristic features of the phase equilibria in such systems. We shall consider individual types of phase equilibria.

Liquid Water–Non-polar Liquid Equilibria

For systems of the first type (see Section II), these equilibria exist in temperature and pressure ranges located on the $p-T$ diagram (Fig.7) above the three-phase curve. For systems of the second type, the equilibria are observed in the region above the critical liquid–liquid curve or above the three-phase curve in Fig.2.

As long as the temperature is not very high and the miscibility of the liquids considered is small, the solutions are dilute and the solubility of the non-polar component in the aqueous phase N_2^w as well as the solubility of water in the non-polar liquid N_1^w obey Henry's law:

$$N_2^w = \frac{1}{H_2^w(p,T)} f_2^n, \qquad N_1^n = \frac{1}{H_1^n(p,T)} f_1^w \qquad (30)$$

The Henry coefficients of non-polar substances in water at low temperatures are anomalously high, which is responsible for the low solubility of non-polar substances in water; the Henry coefficients of water and non-polar substances do not exhibit anomalies. However, apart from the Henry coefficients of the component dissolved in a given phase, the solubility is determined by the fugacity of the component in the phase in equilibrium with the given phase [Eqn.(30)]. At equilibrium between two dilute liquid solutions this fugacity is close to that of the component in the state of the pure liquid. Both pure water and non-polar liquids have in most cases low vapour pressures at low temperatures and hence low fugacities. According to Eqn.(30), this finding is one of the causes of the low miscibilities of the phases under consideration at low temperatures. With increased temperature, the vapour pressures of the pure liquids also increase, which leads to an increase in the miscibility of the liquids. Here one should bear in mind that, as a consequence of the high Henry coefficients of substances dissolved in water, their solubilities in water are in most cases small and the solubilities of water in non-polar substances, characterised by comparatively small Henry coefficients, become considerable. This factor is responsible for some asymmetry in the miscibility of water and non-polar substances.

An increase of pressure reduces the solubility of water in a non-polar liquid. In the region of the applicability of Henry's law this decrease is defined by Eqn.(29) and can be explained by the fact that the molar volume of pure water is much smaller than the partial molar volume of water dissolved in a non-polar substance. The effect diminishes with increase of pressure owing to the diminution of the partial molar volume of water as the pressure increases. As the critical state is approached, the decrease of the solubility of water in a non-polar liquid under the influence of pressure is intensified, since the denominator of Eqn.(29) should then be replaced by $RT\,\partial \ln f_1^n/\partial N_1^n$, which tends to zero at the critical point (and $\partial N_1^n/\partial p$ tends correspondingly to infinity).

The experimental data referring to both the first and second types of water–non-polar substance systems confirm these findings. Thus Fig.14 illustrates the pressure dependence of the water content in decane in equilibrium with liquid water[64]. The closer the state of the system to the critical end point (Fig.4), the sharper the decrease of the water content in the non-polar liquid with increase of pressure. Fig.15 presents the miscibility in the tetrahydronaphthalene–water system[30] (system of the second type); in this case too the influence of pressure on the solubility of water in tetrahydronaphthalene increases sharply as the critical point is approached.

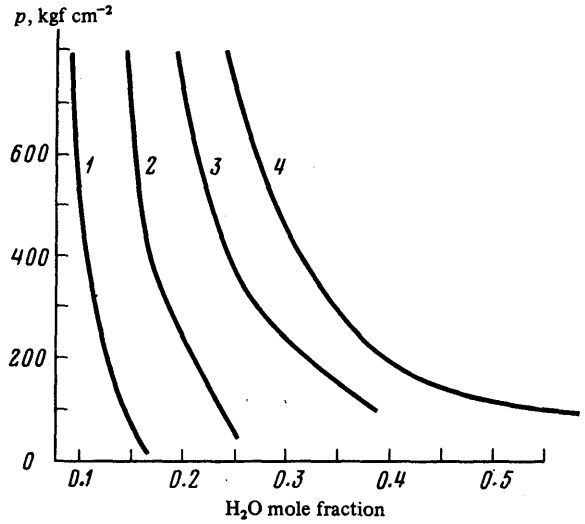


Figure 14. The influence of pressure on the water content in liquid decane in equilibrium with liquid water at different temperatures (°C): 1) 225; 2) 250; 3) 275; 4) 290.

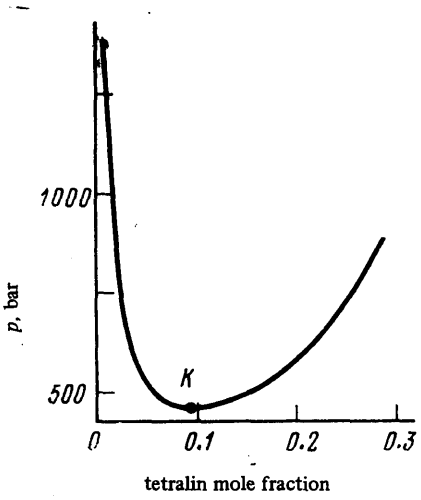


Figure 15. The influence of pressure on the compositions of the equilibrium liquid phases in the tetrahydronaphthalene–water system at 350 °C; *K*—critical point for the liquid–liquid equilibrium.

The solubility of non-polar liquids in water at low and moderate temperatures increases with pressure. This is because at low temperatures the vacancy mechanism of the dissolution[52] of non-polar substances in water plays a major role. In this dissolution mechanism the partial molar volume of the non-polar substances dissolved in water is anomalously small—smaller than the molar volume of the pure liquid non-polar substance. The dissolution of the liquid non-polar substance in water is then accompanied by a decrease of volume and, in conformity with the requirements of thermodynamics, an increase of pressure should promote an increase of solubility. As an example, one may quote data for the water–n-butane system[65]. At high temperatures the vacancy mechanism of dissolution loses its importance and the partial molar volumes of non-polar substances in water increase sharply (see Section IV) and an increase of pressure leads to a decrease of their solubility in water.

Thus at a high temperature the miscibilities of water and a non-polar substance decrease with pressure.

The Non-Polar Liquid–Aqueous Liquid–Gas Phase Three-Phase Equilibrium

If the miscibilities of the liquids are small, then the fugacity of each component in the gas phase in equilibrium with the two liquids is almost equal to the fugacity of this component in the state of the pure liquid. When Dalton's law holds, the pressure in the gas phase of the three-phase state is in this instance almost equal to the sum of the vapour pressures of both components and is therefore higher than the pressure of each component; the composition of the gas phase is intermediate between the compositions of the two liquid phases. The phase diagram then has the form illustrated in Fig.3.

With increase of temperature, the following possibilities for the evolution of the three-phase state exist.

(a) The properties of solutions of water in a non-polar liquid approach those of the gas phase and a critical end point is established (Fig.4). Since the three-phase equilibrium pressure is higher than the vapour pressure of the pure non-polar liquid, the pressure at the critical end point, which belongs to the three-phase equilibrium, is also higher than the vapour pressure of the non-polar liquid. The temperature at the critical end point must be lower than at the critical point of the non-polar substance. For this reason, the branch of the critical curve beginning at the critical point of the pure non-polar substance should be directed towards increasing pressures and decreasing temperatures on the $p-T$ diagram regardless of whether or not the critical temperature of the non-polar substance exceeds the critical temperature of water. Phase equilibria of this kind are characteristic of the first type of water–non-polar substance equilibrium.

(b) The critical end point is established as a result of the mutual approach of the properties of the solution of the non-polar substance in water and of the gas phase. Equilibria of this type are at present unknown.

(c) An azeotrope appears in the system and there is a change of the three-phase equilibrium from the type illustrated in Fig.3 to the type illustrated in Fig.16¶. A characteristic feature of this three-phase equilibrium is that the water content in the gaseous solution is greater than in the

¶If the non-polar substance passes from the solid to the liquid state at an extremely high temperature, there is a possibility of only the three-phase equilibrium of the type illustrated in Fig.16.

liquid aqueous solution. In this case there is a possiblity of the establishment of a critical end point as a result of the mutual approach of the properties of the two liquid phases. The establishment of the critical end point is possible at a temperature below the critical temperatures of both water and the non-polar substance. These features are characteristic of water–non-polar substance systems of the second type (Fig. 2).

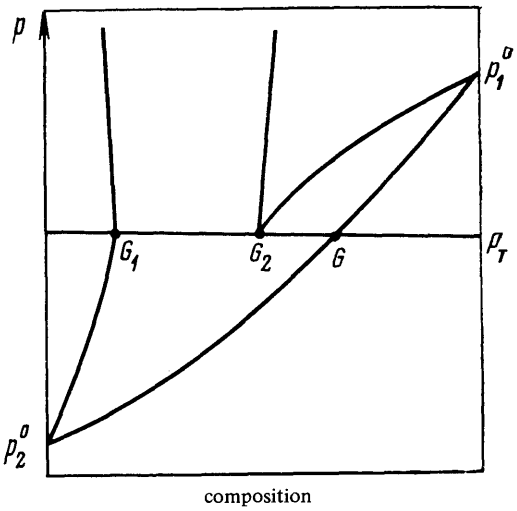


Figure 16. Three-phase equilibrium of the second type; L_1, L_2, and J—compositions of the coexisting liquid and gas phases.

For the above type of equilibria to occur, it is necessary that the content of the non-polar substance in the gas phase should be smaller than in the aqueous solution. For a rough estimate of the possibility of the realisation of this condition, we shall assume that the content of the non-polar substance in the gas phase N_2^g is determined by Dalton's law as the ratio of the partial pressure of the non-polar substance to the sum of the vapour pressures of water (p_1^0) and the non-polar substance (p_2^0):

$$N_2^g = p_2^0/(p_2^0 + p_1^0),$$

and the mole fraction of the non-polar component in the aqueous phase is determined by Henry's law: $N_2^W = p_2^0/H_2^W$. From the condition $N_2^g < N_2^W$, we obtain $H_2^W < p_1^0 + p_2^0$, which requires relatively low values of the Henry coefficient, i.e. a high solubility of the non-polar substance in water. Since a high solubility of the non-polar substance in water is possible at an extremely high temperature, the type of three-phase equilibria under discussion is apparently possible in systems incorporating a non-polar liquid with a high critical temperature and with an increased ability to dissolve in water.

The Aqueous Liquid–Gas Phase Equilibrium

The region of aqueous liquid–gas phase equilibria in systems of the first type is designated by the latter B in Fig. 3, which refers to temperatures below the temperature of the critical end point. Above the temperature of the critical end point (Fig. 4), the aqueous liquid–gas phase equilibrium frequently extends to extremely high pressures. Thus in the water–ethane, water–benzene, water–carbon dioxide, and water–xenon systems equilibria of the above type have been traced up to pressures of $(3–3.5) \times 10^3$ kgf cm^{-2}.

This behaviour of the equilibrium under consideration is observed in a range of temperatures between that of the critical end point and the minimum in the critical temperature. It resembles the behaviour of the aqueous liquid–non-polar liquid equilibrium discussed above, which is reasonable, because, at the terminal critical point of systems of the first type, the non-polar liquid and the gas phase become identical and the resulting phase "inherits" the properties of both phases. At high pressures and low temperatures the properties of the liquid phase are manifested to a greater extent, while at low pressures and high temperatures the properties of the gas phase predominate. As already stated, in the aqueous liquid–non-polar liquid equilibrium the pressure does not promote the mutual approach of the properties of the phases and in the equilibrium between the aqueous liquid and the gas phase at high pressures the compositions of the phases do not approach one another as the pressure is raised.

In systems of the first type, at temperatures exceeding the minimum critical temperature, a critical state arises under certain conditions between the gas and the aqueous liquid when the pressures are low. If the pressure is then increased under isothermal conditions, the system remains homogeneous over a certain range of pressures and then splits into two phases when the pressure attains a sufficiently high value; a further increase of pressure increases the degree of layer formation, as in the non-polar liquid–aqueous liquid equilibrium. Such behaviour is characteristic of the separation of gaseous mixtures of the second kind into layers (Fig. 1*a*). The majority of the water–non-polar substance systems investigated belong to this kind. In systems of the kind described by Fig. 1*b* there are no gas–aqueous liquid critical states at all and, starting from the critical point of water and at higher temperatures, there exist critical states referring to the so-called gas–gas equilibrium.

The gas–liquid critical phenomena beginning at the critical point of pure water in water–non-polar substance systems of the first type are in most cases possible over a short range of temperatures between the critical temperature of water and the minimum critical temperature. For paraffinic hydrocarbons, the minimum critical temperature does not fall below 350 °C, while for mixtures of water and aromatic hydrocarbonds it is lower (294 °C in the case of benzene).

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Simple two-parameter equations of state (van der Waals and Redlich–Kwong) reproduce qualitatively the characteristics of the phase equilibria in the water–non-polar substance systems[66]. The quantitative agreement between the calculations and experiment is unsatisfactory, particularly for the van der Waals equation.

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Reactions of Acetylene in Superbasic Media

B.A.Trofimov

The results of studies of fundamentally new reactions of acetylene and its substituted derivatives in media of very high basicity are surveyed. They lead to hitherto unknown or relatively inaccessible monomers, reagents, and intermediates: 2-vinyloxybuta-1,3-diene, pyrroles, and *N*-vinylpyrroles, divinyl sulphide, divinyl telluride, 4-methylene-1,3-oxathiolan, di(buta-1,3-dienyl) sulphide, dihydrothiophen, 1-vinyl-2-thiabicyclo[3,2,0]hept-3-ene, etc.
The most important properties of superbasic media consisting of an alkali metal hydroxide and a dipolar aprotic solvent as well as the probable mechanisms of their activating effect on anions and the triple bond are examined. An attempt is made to analyse these reactions in terms of coordination catalysis by alkali metal cations.
The bibliography includes 199 references.

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I. INTRODUCTION

As one of the key types of chemical raw material, acetylene, which was somewhat eclipsed in the 1960's by petrochemical ethylene and propene, is now again attracting the attention of investigators and technologists because of the progressive increase in the cost of petroleum and gas in the work markets[1].

As a result of the development of plasma, laser, and ultrasonic techniques, cheap acetylene will soon be obtainable not only from the petroleum raw material but also from different kinds of coal and combustible shale[2]. Research programmes designed to create a plasma technology for the direct synthesis of acetylene from coal are being developed[3]. Successful studies are being made[4] on the utilisation of liquid acetylene for technological purposes.

The majority of chemical reactions of acetylene are known not to require a supply of energy and are in fact accompanied by its evolution. There are many reasons why acetylene should become in the future the sole raw material for industrial organic synthesis[5]. It has been calculated[6] that acetylene obtained from calcium carbide already constitutes a realistic alternative to the petroleum raw material. On the other hand, a fall in the consumption of ethylene has been noted; for example, in 1978 the ethylene factories in the USA failed to utilise almost half their capacity[7].

A further development of the foundations of the chemistry of acetylene, laid as early as the beginning of this century by Academician A.E.Favorskii, has therefore become an urgent necessity. A new field—the chemistry of acetylene in super basic media—is rapidly developing on the basis of Favorskii's research[8]. In the present review an attempt is made to summarise the main results obtained in this field.

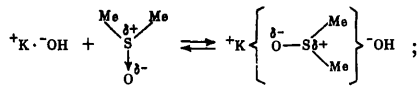
II. THE GENERATION AND CERTAIN CHARACTERISTICS OF SUPERBASIC MEDIA

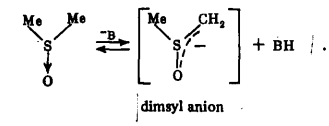
Superbasic media include those consisting of a strong base and a solvent or reagent capable of specific binding of the cation, "baring" the anion[8,9]. Superbasic systems can be obtained on the basis of linear and cyclic glycol ethers, macrocyclic polyethers (crown-ethers), dipolar aprotic solvents such as dimethyl sulphoxide (DMSO), sulpholane, hexamethylphosphoramide (HMP), and phosphine oxides, as well as amides, liquid ammonia, amines, etc. For example, the basicity of sodium methoxide in 95% DMSO is higher by 7 orders of magnitude than in pure methanol[10]:

0.025 M $NaOCH_3$	
Solvent	Acidity function H_
Methanol	12.2
95% DMSO + 5% methanol	19.4

A particularly dramatic increase of basicity occurs at the maximum concentrations of a dipolar aprotic solvent. Thus tetramethylammonium hydroxide in 99.5% aqueous DMSO is more basic by 14 orders of magnitude than in pure water[11].

The superbasicity of the KOH–DMSO system is caused to a first approximation by the separation of the ion pair of the base[12] and by the formation of the highly basic and little solvated dimsyl anion[9] (B^- is a strong base):



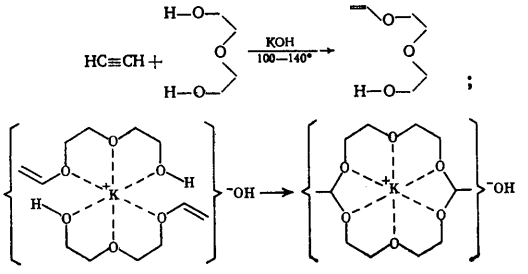


However, this does not exhaust the role of DMSO. In the general case account must be taken of cooperative effects involving changes in factors such as the dielectric constant of the medium, hydrogen bonding, the activity of water, dispersion interactions, and changes in the structure of water and in the degree of ion hydration[11,13,14].

The situation arising under the conditions of interfacial catalysis[15,16], where one of the phases is highly concentrated alkali and hydroxide ions are transferred by bulky organophilic cations incapable of forming a contact ion pair, can also be regarded as superbasic.

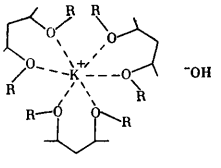
The significant acceleration of the nucleophilic addition to the triple bond in media specifically solvating the cation was first noted in a study of the vinylation of poly(ethylene glycol).[17] As a result of the chelation of the potassium cation

by poly(ethylene glycol) chains, side reactions involving the cleavage and disproportionation of the poly(ethylene oxide) fragments[18,19] and probably also "template" heterocyclisation, leading to macrocyclic crown-like acetals, which, together with linear oligomers, accelerate the process



autocatalytically, are characteristic of reactions of this kind.

The catalytic effects of the side products of the vinylation of monohydric alcohols[20,21]—low-molecular-weight thermopolymers of alkyl vinyl ethers $-[-CH_2-CH(OR)-]_n-$—also capable of chelating the cations, are apparently of the same type:



These studies led to the development and industrial application of a new technology for the vinylation of butanol at atmospheric pressure[20,21] and to the intensification of the processes involving the vinylation of diethylene glycol[22] and ethanolamines[23], which are nowadays carried out on an experimental industrial scale.

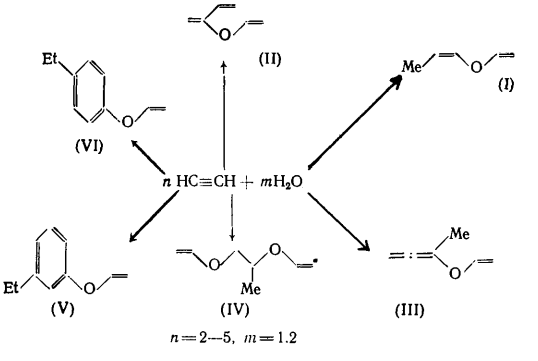
In aprotic dipolar solvents (DMSO, HMP, and methylpyrrolidinone) in the presence of catalytic amounts of alkali, primary alkanethiols add to acetylene even at atmospheric pressure and at a temperature of 10–20 °C, forming vinyl sulphides in 60–90% yield (reaction time 1 h),[24] which corresponds to an increase of the reaction rate by many orders of magnitude. Tertiary and aromatic thiols, which are more difficult to vinylate, react with acetylene much more readily in systems of this kind than under the usual conditions (30–50 °C, 10–15 atm).

Thus in superbasic media in the presence of "bared" anions of strong bases (alkalies, alkoxides, amides, and alkali metals) the nucleophilic addition to the triple bond is very greatly facilitated. However, a much more significant factor is that fundamentally new reactions become possible under these conditions. There exist fundamental thermodynamic grounds for this. Thermodynamic measurements have shown[25] that in aprotic dipolar solvents the free energy of the anions increases sharply and as a result they are converted into supernucleophiles. It is very significant that the activity of weak nucleophiles then increases to a much greater extent than that of strong nucleophiles. For example, on passing from ethanol to DMSO, the relative increment of the Gibbs free energy of the phenoxide anion (a fairly weak nucleophile) is greater by 10 kcal mol^{-1} than for the phenylsulphide anion, which is a stronger nucleophile[25].

III. HYDRATION OLIGOMERISATION OF ACETYLENE

The characteristics of superbasic systems discussed above are responsible for the successful addition to acetylene even of a comparatively weak nucleophile such as the hydroxide ion, the low activity of protons characteristic of such systems inhibiting the prototropic transformation of the intermediate vinyloxide anion into acetaldehyde. However, it has not so far been possible to observe the formation of divinyl ether under these conditions. Instead of this natural pathway, a series of completely unusual reactions have been observed[8,26–31] in the DMSO–KOH system, which proceed under extremely mild conditions (80–120 °C) and which can be combined under the common name "hydration oligomerisation of acetylene" (Scheme 1).

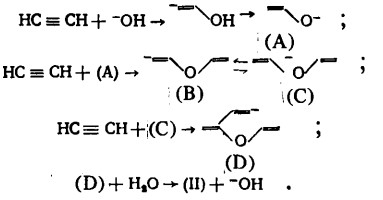
Scheme 1



The simplest oligomer obtained under these conditions is a methylated hydratodimer—1-*cis*-propenyl vinyl ether[26] (DMSO acts as a methylating agent).

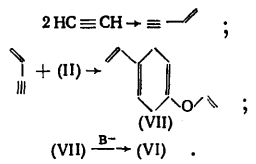
This is followed by the following substance in order of increasing complexity: a hydratotrimer—2-vinyloxybuta-1,3-diene (II) [8,27,29–31] and its allene isomer—3-vinyloxybuta-1,2-diene (III),[30] a methylated dihydratotrimer—1,2-di(vinyloxy)-propane (IV),[28,30] and finally hydratopentamers—*meta*- and *para*-ethyl(vinyloxy)benzenes (V) and (VI).[30] The yields are in general low; however, they depend significantly on the composition and nature of the superbasic catalytic system, particularly on the nature of the cation and the solvent and also on buffer additives such as alkali metal phosphates, which regulate the proton transfer processes. Conditions have been found[27,29,30] under which 2-vinyloxybuta-1,3-diene—one of the most interesting products of the hydration oligomerisation of acetylene—is obtained in a yield greater than 70%. The yields of other hydrato-oligomers can apparently also be increased to a preparatively acceptable level when necessary.

One of the possible ways of forming vinyloxybutadiene involves a multistage "threading" of three acetylene molecules onto the hydroxide ion:



A weak feature of this scheme is the assumption of a prototropic rearrangement of the vinyloxyvinyl β-carbanion (B) to the corresponding α-carbanion (C), which is in all probability less stable owing to the strong repulsion of the charge from the unshared electron pairs of the oxygen atom.

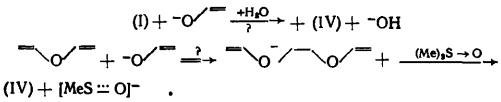
The ethyl(vinyloxy)benzenes (V) and (VI) could be regarded as products of the diene condensation of vinyloxybutadiene (II) and the intermediate vinylacetylene, which is completed by the prototropic rearrangement of the primary vinylcyclohexadiene adduct (VII):



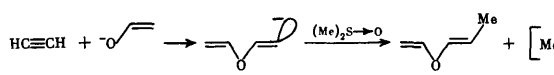
(VII) $\xrightarrow{B^-}$ (VI) .

However, ethyl(vinyloxy)benzene could not be obtained by the direct interaction of authentic vinylacetylene and vinyloxybutadiene (II).[29]

It is just as difficult to interpret the formation of 1,2-di(vinyloxy)propane (IV), because it is necessary to assume the highly unlikely nucleophilic addition of the vinyloxide anion to propenyl vinyl ether (I) or to divinyl ether:



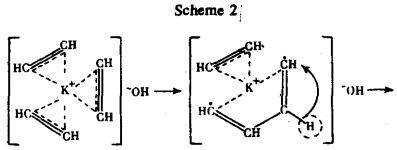
Concluding the enumeration of facts which cannot be acceptably explained within the framework of generally accepted ideas, it is necessary to draw attention also to the configuration of 1-*cis*-propenyl vinyl ether (I). In nucleophilic addition to acetylenes, the intermediate anions usually have the *anti*-configuration, in which the repulsion of the charge and the unshared electron pairs of the heteroatom is a minimum[32]. The formation of the *trans*-isomer rather than the *cis*-isomer of the ether (I) was therefore to be expected:

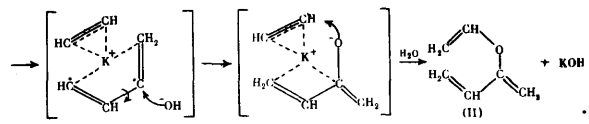


The complete *cis*-stereoselectivity in this case is evidence against simple nucleophilic attack by the vinyloxide anion on the triple bond. Evidently the reactions illustrated in Scheme 1 require other explanations. It was noted above that in superbasic media the anions become supernucleophiles as a result of desolvation and the separation of ion pairs under the influence of strong dipoles (solvent molecules). However, the same factors should also alter the electrophilic activity of the cation. In a system with a markedly reduced activity of water an alkali metal cation, lacking its usual hydration shell and separated by a solvent molecule from its anion, should attempt to compensate for its desolvation by coordinating to some extent to other nucleophiles present in the system, in the given instance acetylene molecules, formally in the same way as in the case of transition metal cations[33]. The coordination leads to the withdrawal of the π-electron density of the acetylene ligands to the cation and the consequent increase of the sensitivity of the triple bonds of the ligands to a nucleophilic attack.

One of the possible mechanisms of such coordination catalysis, involving a partly dehydrated potassium cation in the hydration trimerisation of acetylene, is illustrated in Scheme 2:

Scheme 2





This scheme explains the observed marked dependence of the result of the reaction on the nature of the coordinating cation and predicts the possibility of obtaining benzene (a nonhydrated acetylene trimer) on decrease of the concentration of water in the system. Benzene and toluene (in the DMSO–KOH system) have indeed been detected in the reaction mixtures—in some cases up to 20% and more[34]. The formation of toluene indicates yet again the ability of DMSO to methylate carbanions under these conditions.

The cyclotrimerisation of acetylene is known to take place smoothly only in the presence of transition metal complexes[35]. Methods for the formation of stable adducts of acetylenes with dehydrated alkali metal hydroxides were patented[36,37] several decades ago. It has been stated in a patent[37] that the absorption of acetylene by potassium hydroxide in 1,1-dibutoxyethane increases sharply with increase of temperature, reaching 0.5 mole per mole of KOH at 75–90 °C, which is three times more than at temperatures between −10° and 0 °C. We are therefore dealing with the chemical interaction of acetylene with KOH and not with its simple dissolution. The important role of such complexes, as key intermediates in certain versions of the Favorskii ethynylation[38–41] and vinylation[42] reactions as well as selective hydrogenation[43–45] of acetylenic alcohols and glycols was demonstrated later. In many instances[38–40,45] these complexes were isolated and investigated. Compared with KOH, sodium hydroxide binds acetylene less strongly, while LiOH does not form complexes with acetylene at all according to Tedeschi et al.[45]

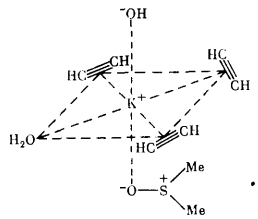
Unfortunately very few experimental data have been published hitherto concerning the nature and structure of the adducts of acetylene and alkali metal hydroxides. It has been reported only that the infrared spectra of complexes of KOH with acetylene[39] and acetylenic alcohols[38] or glycols[38] do not exhibit the usual C≡C and ≡C–H vibrational frequencies, while the O–H stretching vibration band (in the case of alcohols and glycols) is broadened and weakened. On this basis, it was concluded[38,39] that the potassium cation is involved in complex formation reactions with both the π-electrons of the acetylenic linkage and with the oxygen atoms of the hydroxy-groups. In the same study[38–41] evidence is presented showing that the adducts of acetylene with alkali metal hydroxides are chemically fundamentally different from acetylides. According to data obtained by ion-cyclotron resonance and high-pressure mass spectrometry[46], acetonitrile ($CH_3C{\equiv}N$), which is a full electronic analogue of methylacetylene, has a higher chemical affinity for the potassium cation than bases such as ammonia, amines, water, and ethers. Quantum-chemical calculations by the *ab initio* method have shown that this is wholly due to the unexpectedly large contribution of the polarisation of the CH_3CN molecule to the overall energy of its reaction with the cation[47]. Acetylenic compounds should exhibit an equally high affinity for the K^+ cation and an equally marked polarisability under its influence.

Another familiar group of acetylene complexes of alkali metals is derived from acetylides. For example, the oligomerisation of acetylenes under the influence of alkali metals begins with the formation of complexes of acetylides with the initial acetylenes[48–51]. Adducts of phenylacetylides with alkali metals, which are of a radical-ion type and actively initiate the polymerisation of vinyl monomers, have also been isolated recently[52].

According to calculations by the CNDO method[53], preference should be given to an octahedral hydration shell for alkali metal cations with a pronounced electron transfer from oxygen to the metal; the energy gain relative to other possible hydrates then ranges from 24 to 140 kcal mol^{-1}. The charge transfer in such aquo-complexes has been confirmed also by complete theoretical calculations[54]. According to experimental data[55], the sodium cation in the DMSO–dioxan mixture is surrounded by six donor molecules. It is well known that the most stable complexes with potassium cations are formed by crown-ethers containing six oxygen atoms[56].

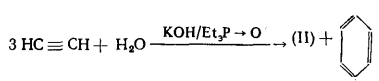
All this justifies the hypothesis that in superbasic catalytic systems a proportion of the usual ligands in the solvation shells of alkali metal cations can be substituted by acetylene molecules, which begin to interact both with one another and with the remaining ligands as a consequence of spatial proximity, polarisation, and partial covalent binding (charge transfer).

The formation of the acetylene hydratotrimers (II)–(IV) can be easily explained by the interaction of ligands, for example, in the following octahedral complex[28]:

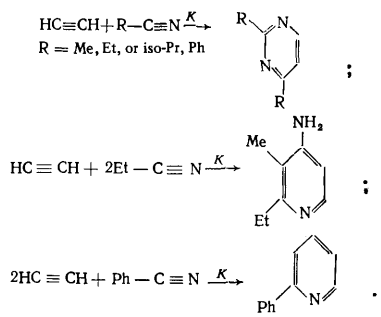


The hydratopentamers (V) and (VI) can be constructed on the same template, provided that two heteroatomic ligands (including DMSO) are replaced by acetylene molecules. Naturally, in real systems there must be a continuous variable spectrum of similar complexes, differing not only in the combinations of the ligands but also in solvation numbers.

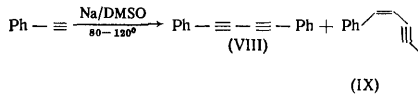
In conclusion of this section, it must be emphasised that DMSO does not constitute the only basis for catalytic systems propagating the reactions under consideration. The superbasic pair KOH–triethylphosphine oxide also catalyses the hydration trimerisation of acetylene. In this case the yield of 2-vinyloxybuta-1,3-diene (II) is 50% and the catalytic reaction mixture contains more than 20% of benzene[34]:



The heterocyclisation of acetylene with nitriles to form pyrimidines and pyridines (1–2% K, 175–200 °C, 13–17 atm, 6–8 h) is known[57]:



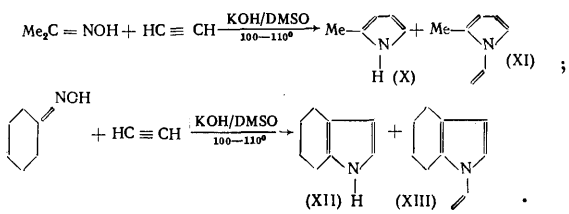
The catalytic system is prepared by the cautious dissolution of metallic potassium in the corresponding nitrile. The yields of 2,4-dialkylpyrimidines and the isomeric 4-aminopyridines are in the range 8–12% (relative to the nitrile which has reacted), but 2,4-diphenylpyrimidine was synthesised in 29–51% yield. The formation of a 2-substituted pyridine was observed only for R = Ph (yield 1.8%). These reactions have now been given a theoretical basis in the light of data[46,47], already quoted, concerning the strong specific interaction of the potassium cation with acetonitrile molecules[46], including their extensive polarisation[47]. The recently discovered[58] dimerisation of phenylacetylene under the influence of a small amount of sodium in DMSO or HMP can also be included in the group of new catalytic reactions under consideration:



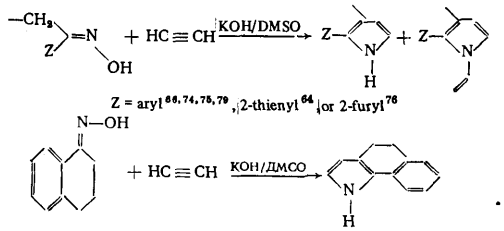
The yield of dimers (VIII) and (IX) reaches 43 and 14% respectively. Other conditions being equal, there is no dimerisation in benzene. Although the oxidative and "additive" dimerisation of acetylenes is well known[59], it has been believed hitherto that these processes can be catalysed only by copper salts.

IV. REACTIONS OF ACETYLENE WITH OXIMES AND AMIDES

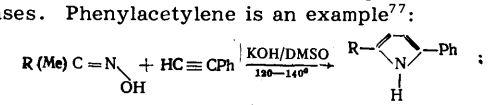
The reaction of acetylene with ketoximes, catalysed specifically by the KOH–DMSO superbasic pair and leading to pyrroles and *N*-vinylpyrroles, was discovered at the beginning of the 1970's.[60,82] For example, 2-methylpyrrole (X) and 2-methyl-1-vinylpyrrole (XI) are formed from acetone oxime[72] while cyclohexanone oxime gives rise to 4,5,6,7-tetrahydroindole (XII) and its 1-vinyl derivative (XIII):[60,67–68,73,78]:



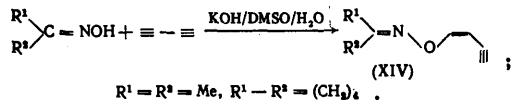
The process proceeds easily and smoothly even at 80–120 °C at atmospheric pressure, being accompanied by a small exothermic effect. The yields of pyrroles are on average 70–80%, reaching 90% and more in certain cases[72,81]. The reaction is of a general type: it involves virtually all ketoximes having at least one CH_2 group in the α-position relative to the oxime functional group, including aromatic[66,74,75,79], heteroaromatic[64,76], and annelated[70] oximes:



Positive results are to be expected when the reaction is extended to certain substituted acetylenes incapable of prototropic isomerisation and stable in the presence of strong bases. Phenylacetylene is an example[77]:



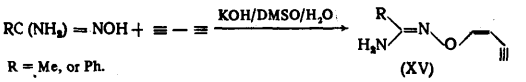
O-Ethynylvinyl derivatives of oximes (XIV) were isolated in 38–41% yield in the reaction with diacetylene instead of the expected 2-ethynylpyrroles[83]:



(XIV)

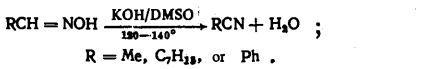
$R^1 = R^2 = Me$, $R^1 - R^2 = (CH_2)_4$.

Under the same conditions, amidoximes react similarly with diacetylene, forming *O*-ethynylvinyl derivatives (XV) in 21–25% yield[84]:



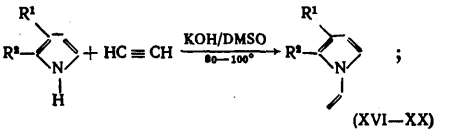
R = Me, or Ph. (XV)

In contrast to ketoximes, aldoximes do not give rise to pyrroles on interaction with acetylene in the KOH–DMSO system, since they are dehydrated to the nitriles[85–87] (yield 65–92%):



$R = Me, C_7H_{15}$, or Ph .

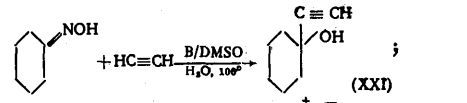
A secondary result of the study of the reactions of ketoximes with acetylene was the development of an effective method for the vinylation of pyrroles at atmospheric pressure[88,89], which is evidently suitable also for the vinylation of other NH-heterocycles. The formation of *N*-vinyl derivatives (XVI)–(XX) in the presence of the KOH–DMSO superbasic pair proceeds under mild conditions (80–100 °C) in 75–95% yield:



(XVI–XX)

$R^1 = Me$, $R^2 = Et$ (XVI); $R^1 = Pr$, $R^2 = Bu$ (XVII);
$R^1 - R^2 = (CH_2)_4$ (XVIII); $R^1 = H$, $R^2 = Ph$ (XIX);
$R^1 = H$, $R^2 = MeOC_6H_4$ (XX) .

In aqueous DMSO the synthesis of pyrroles from ketoximes and acetylene is accompanied by the formation of α-acetylenic alcohols[90]. For the ratio H_2O : DMSO = 1 : 2 (by volume) and at 100 °C, the yield of 1-ethynyl-1-cyclohexanol (XXI) is 47%:[76]



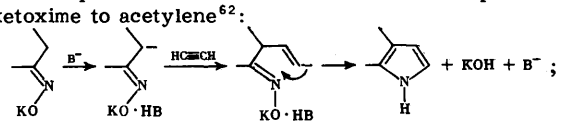
(XXI)

B = NaOH, KOH, RbOH, or $[(Bu)_4\overset{+}{N}]\overline{O}H$.

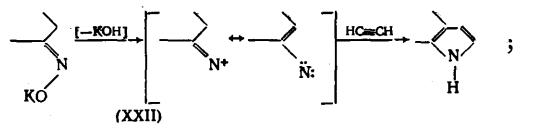
This reaction also proceeds in dioxan and dioxan–DMSO mixtures[90].

The mechanism of the formation of pyrroles from ketoximes and acetylene is not as yet entirely clear. The key stage of the reaction could be one of the following:

(a) nucleophilic addition of the carbanionic component of the ketoxime to acetylene[62]:

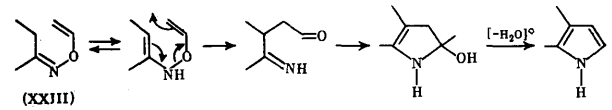


(b) 1,3-dehydration of the ketoxime and the addition of the 1,3-dipole (XXII) (or the corresponding vinylnitrene) to the triple bond[62,65,87]:



(XXII)

(c) sigmatropic rearrangement of the intermediate *O*-vinyloximes (XXIII):[90]

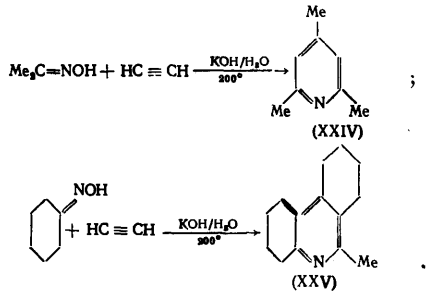


(XXIII)

So far there is no reason to reject only the last mechanism: the *O*-vinyloximes isolated in a low yield on thermolysis in the absence of acetylene do not give rise to pyrroles[92]. Furthermore, as mentioned above, the reaction involving phenylacetylene results in the formation of 5-phenylpyrroles, while the rearrangement of the intermediate (XXIII) should have resulted in the introduction of the phenyl group in the 4-position in the pyrrole ring (nucleophiles add to the terminal carbon atom of phenylacetylene)[32].

The systematic development of this new field, which has arisen at the boundary between the chemistries of acetylene and pyrrole, is being continued[93–106]. The data accumulated show convincingly that the reaction under consideration constitutes at present one of the simplest and most effective methods of synthesising pyrrole systems.

It is of interest that in an aqueous medium without DMSO the base-catalysed interaction of acetylene with ketoximes proceeds quite differently: instead of pyrroles, pyridines are formed[87,107]. For example, symmetrical collidine (XXIV) is obtained from acetoxime, and 9-methyloctahydrophenanthridine (XXV) is formed from cyclohexanone oxime:

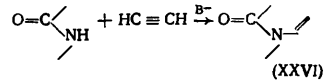


(XXIV)

(XXV)

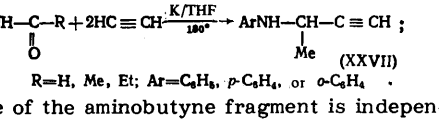
The yield of pyridines is 20–30%, but so far no attempt has been made to optimise this new and extremely promising reaction.

The vinylation of carboxylic acid amides with acetylene in the presence of bases leads to *N*-vinylamides (XXVI):[108–110]



(XXVI)

However, if the catalyst of this reaction is obtained by dissolving metallic potassium in a mixture of an anilide and tetrahydrofuran (THF) or dioxan, then 3-arylamino-1-butynes (XXVII) are formed from these reagents in yields up to 47% together with *N*-vinyl derivatives (XXVI).[111,112] Like the potassium derivatives of anilides obtained via alkoxides, the analogous sodium system does not catalyse the reaction:



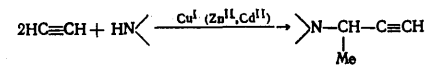
(XXVII)

R=H, Me, Et; Ar=C_6H_5, *p*-C_6H_4, or *o*-C_6H_4 .

The structure of the aminobutyne fragment is independent of the substituent R, which means that the acid component of the anilide is split off, being replaced by the acetylene dimer.

The optimisation of the reaction[113] by mathematical design made it possible to suppress vinylation almost completely, maintaining the yield of acetylenic amines (XXVII) at the level of 35%. It was established that the formation of the

catalyst involves the reductive cleavage of the anilide, one of the products being potassium arylamide (ArNHK), which belongs to the class of superbases[114–118]. It was believed that the familiar reaction of acetylene with secondary amines, resembling to some extent the reaction considered here and leading to the same aminobutynes, proceeds only in the presence of transition metal salts[119]:



However, recently† an analogous reaction between acetylene and aniline was achieved also in the presence of potassium anilide:

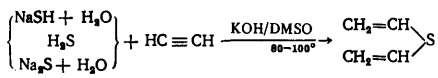
$$PhNH_2 + 2HC\equiv CH \xrightarrow{PhNHK} PhNHCH(Me)C\equiv CH$$

The yield of 3-phenylaminobut-1-yne was ~24%, while the degree of conversion of aniline was 21% (160 °C, 12 atm C_2H_2, 2 h, dioxan). The reaction proceeds with approximately the same yield (25%) albeit with a higher degree of conversion of aniline (41%) when it is catalysed by the specially prepared copper acetylide (20–60 °C, 14 atm C_2H_2 + 3 atm N_2, ethanol–acetic acid)[120].

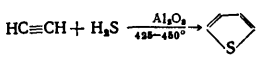
Thus a certain parallelism in the type of activation of acetylene by alkali metal cations under superbasic conditions and metal complexes is again revealed.

V. OLIGOMERISATION OF ACETYLENE WITH PARTICIPATION OF SULPHUR-CONTAINING NUCLEOPHILES

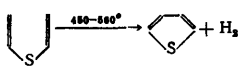
The reactions of acetylene with sulphur-containing nucleophiles are no less varied and unexpected in superbasic media. The simplest of these nucleophiles, the sulphide ion generated from hydrogen sulphide in the presence of an excess of alkali or from alkali metal sulphides in DMSO, adds under very mild conditions (at a temperature of only 80° to 100 °C) and almost quantitatively (under optimum conditions) to two acetylene molecules, forming divinyl sulphide[121–125]:



This at first sight simple and evident reaction has its history. At the beginning of the century the high-temperature catalytic addition of hydrogen sulphide to acetylene was investigated by Chichibadin[126,127], but he obtained thiophen instead of divinyl sulphide:

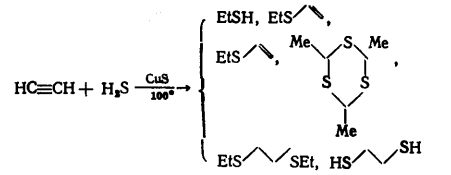


Subsequently investigators frequently returned to this synthesis using as catalysts metal sulphides[128–130], nickel and cobalt on alumina[131], and an aluminolanthanochromium catalyst[132], but the formation of divinyl sulphide was never mentioned. It has been shown recently that at high temperatures divinyl sulphide is thermodynamically unstable and is dehydrocyclised to thiophen[133]:

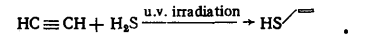


† See B.A.Trofimov, S.F.Malysheva, and E.P.Vyalykh, Zhur.Org.Khim., 15, 880 (1979).

Towards the end of the 1930's, Reppe again attempted to synthesise divinyl sulphide from acetylene and hydrogen sulphide. He obtained a complex mixture of organosulphur products[134,135], but divinyl sulphide was not present among them:



When a mixture of acetylene and hydrogen sulphide in the liquid phase (−78 °C) or in the gas phase (20 °C) is irradiated with ultraviolet light, ethylenethiol is formed in 33% yield[136]:

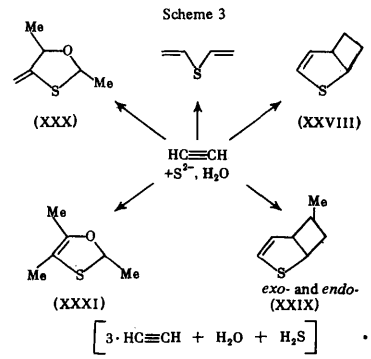


The homologues of acetylene react similarly, the yield of propenethiols (from methylacetylene) amounting to 87%.[136]

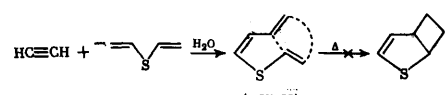
Thus neither high-temperature nor photochemical initiation nor heterogeneous catalysis permit the direct synthesis of divinyl sulphide from acetylene and hydrogen sulphide. This monomer has been obtained by multistage reactions via mustard gas[137–142], di(2-bromoethyl)sulphide[143–145], or thiodiglycol[146–148]. Until recently, it was therefore only of strictly theoretical interest. The reaction of acetylene with the sulphide ion in a superbasic medium made divinyl sulphide a very readily available and cheap product, which can now be manufactured industrially on any scale.

As in the case of the hydroxide ion, the addition of sulphide anions to acetylene in superbasic media is accompanied by unusual heterocyclo-oligomerisation reactions (Scheme 3). Thus the reaction in the NaOH–DMSO–H_2O system yields, together with divinyl sulphide, a new bridged heterocycle—2-thiabicyclo[3,2,0]hept-3-ene (XXVIII) and its *exo*- and *endo*-6-methyl derivatives (XXIX),[149–151] which are in essence thiylated trimers, as well as 2,5-dimethyl-4-methylene-1,3-oxathiolan (XXX) and its endocyclic isomer 2,4,5,-trimethyl-1,3-oxathiol (XXXI),[152–155] made up of three acetylene molecules, a hydrogen sulphide molecule, and a water molecule:

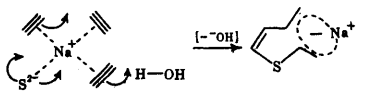
Scheme 3



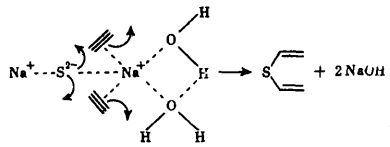
Evidently template cyclisation again takes place under these conditions. The dark [2 + 2]-cyclisation of the probable intermediate 1-vinylthiobuta-1,3-diene (XXXII) is prohibited by orbital symmetry rules:



However, in the electric field of the coordinated cation, where the π-symmetry of the ligands is violated, the prohibition of cyclisation is removed:



One cannot rule out the possibility that the divinyl sulphide molecule (which in this context can be regarded as a sulphur-containing acetylene dimer) is also produced by a single-stage process in the initial matrix:



One of the roles of DMSO under these conditions may involve the partial dehydration of the Na^+ cation as a result of the formation of stable complexes of the type $Me_2SO.2H_2O$ [156,157] as well as hydrogen bonds between H_2O and DMSO molecules, which are stronger than in the self-associated water species[158].

The second order of the reaction with respect to phenylacetylene in the synthesis of di(2-phenylvinyl)sulphide (XXXIII) from phenylacetylene and hydrated sodium sulphide in DMSO, HMP, and triethylphosphine oxide may be regarded as the kinetic confirmation of the reality of the "template effect":[159]

$$PhC\equiv CH + Na_2S\cdot 9H_2O \xrightarrow{80\text{–}100^\circ} Ph\!\!\diagup\!\!\diagdown S\!\!\diagup\!\!\diagdown Ph \quad (XXXIII)$$

Such formal kinetics are characteristic of many metal complex reactions of acetylene via a coordination mechanism[160]. The activation parameters—the unusually low energy barrier ($\Delta H^{\neq} \cong 7$ kcal mol^{-1}) accompanied by an enormous decrease of entropy ($\Delta S^{\neq} \cong -50$ e.u.)—are consistent with this mechanism; thus the transition state of the reaction does indeed have a highly ordered structure and the dissociation and formation of bonds are to a large extent synchronised. When the reaction was followed by ^1H NMR over a wide range of conversions (up to 70%), the splitting of the signals due to the olefin protons, which might have been caused by the formation of an intermediate 2-phenylvinyl sulphide anion in the case of a multistage addition of the sulphide ion to two phenylacetylene molecules, was not observed[159].

Yet another property is characteristic of superbasic catalytic systems, which distinguishes them from typical metal complex catalysts, namely the outcome of the reaction frequently depends fundamentally on the nature of the components of these systems. Thus, when DMSO is replaced by HMP, it is possible to select conditions for the reaction of acetylene with hydrogen sulphide[161] such that its only product is ethanethiol:

$$HC\equiv CH + H_2S \xrightarrow[90^\circ]{KOH/HMP} \begin{cases} \diagup\!\!\diagdown S\!\!\diagup\!\!\diagdown \\ EtSH \end{cases}$$

This synthesis is of fundamental importance, because it illustrates strikingly the ability of certain superbasic systems to stimulate oxidation-reduction processes of the type

$$\diagup\!\!\diagdown S^- + H_2S \xrightarrow{KOH/HMP} EtS^- + S$$

In a superbasic system involving DMSO or HMP the cyclic octamer of elemental sulphur is readily cleaved already at 80 °C, forming as a result of reaction with acetylene the same product as the sulphide ion; the main product is divinyl sulphide[29,162,163], which can be obtained in 75–80% yield by this reaction:

$$HC\equiv CH + S_8 \xrightarrow{KOH/DMSO/H_2O} \diagup\!\!\diagdown S\!\!\diagup\!\!\diagdown$$

The elemental sulphur–alkali metal hydroxide–DMSO system was later proposed[163] as a new reagent for the synthesis of organosulphur compounds from organic halides. Analogous direct oxidation-reduction vinylation reactions proved to be possible also for elemental selenium[27,29,31] and tellurium[29,164–166]. The latter reacts more effectively in HMP. The yield of divinyl derivatives (XXXIV) and (XXXV) is greater than 50%:

$$HC\equiv CH + Se_\alpha \xrightarrow[95\text{–}120^\circ]{KOH/DMSO/H_2O} \diagup\!\!\diagdown Se\!\!\diagup\!\!\diagdown \quad (XXXIV)$$

$$HC\equiv CH + Te \xrightarrow[110\text{–}120^\circ]{KOH/HMP/H_2O} \diagup\!\!\diagdown Te\!\!\diagup\!\!\diagdown \quad (XXXV)$$

The direct synthesis of divinyl selenide (XXXIV) and divinyl telluride (XXXV) from the elements and acetylene leads to interesting prospects for the development of the chemistry of unsaturated organoselenium and organotellurium compounds.

The reactions with alkali metal polysulphides, which also proceed with the cleavage of the polysulphide chain and the formation of divinyl sulphide in 70–92% yield[167], are closely related to the above group of oxidation-reduction processes:

$$HC\equiv CH + Na_2S_n \xrightarrow[100^\circ]{KOH/DMSO/H_2O} \diagup\!\!\diagdown S\!\!\diagup\!\!\diagdown \quad n = 2-4$$

In the reaction with organic disulphides acetylene is readily inserted in the S–S bond, forming *cis*-1,2-di(organylthio)-ethylenes (XXXVI) in 60–80% yield:[168–170]

$$HC\equiv CH + \begin{matrix} R & S \\ S & R \end{matrix} \xrightarrow[120^\circ]{t\text{-}BuOK/DMSO} \begin{matrix} R & & R \\ S & & S \end{matrix} \quad (XXXVI)$$

R=Alk or Ph.

If favourable conditions are created at the same time for the transfer of a proton (for example, by adding H_2O to the system), alkyl vinyl sulphides are also formed[171–174] in a yield which can be raised to 80%:[172]

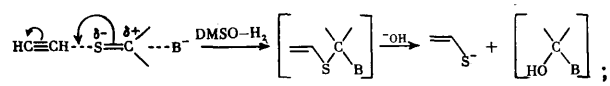
$$HC\equiv CH + \begin{matrix} Alk & S \\ S & Alk \end{matrix} \xrightarrow{KOH/H_2O} \diagup\!\!\diagdown S\!\!\diagup\!\!\diagdown Alk$$

The ease of cleavage of the S–S bond under these conditions hinders the synthesis of divinyl polysulphides. However, they are probably nevertheless formed as intermediates, as shown by the formation of 1,2-di(vinylthio)ethylene (XXXVII) from acetylene and sodium disulphide[155,167,175]:

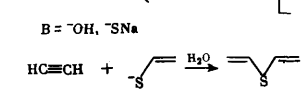
$$HC\equiv CH + Na_2S_2 \xrightarrow[80^\circ]{KOH/DMSO/H_2O} \diagup\!\!\diagdown S\!\!\diagup\!\!\diagdown S\!\!\diagup\!\!\diagdown$$

$$\left[\diagup\!\!\diagdown S\!\!\diagup\!\!\diagdown S\!\!\diagup\!\!\diagdown\right] + HC\equiv CH \quad (XXXVII)$$

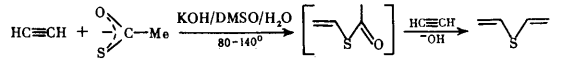
Unusual reactions of acetylene with thione systems—carbon disulphide[177,178], thiourea[176,179,180], dithiocarbamate[176,181–184] and phosphorothioate[185] esters and salts, and even sodium thiosulphate[176]—take place readily in a superbasic medium[176]. As a result of its high polarisability, the thione fragment behaves under these conditions as a powerful uncharged nucleophile. Ultimately the series of successive (or synchronous) addition and substitution steps usually leads to divinyl sulphide (yield 70–80%):



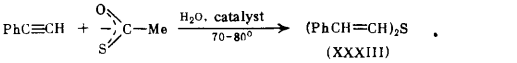
B = ^-OH, ^-SNa



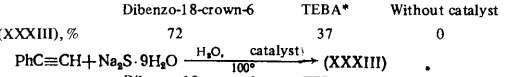
Under superbasic conditions, extremely weak nucleophiles such as the thioacetate anion, add readily to the triple bond[182,184,186], although previously they were believed to be incapable of this:



The yield of divinyl sulphide by this reaction is 60%.[186] The same reaction with phenylacetylene served as one of the examples used to demonstrate for the first time that interfacial catalysis by crown-ethers and tetraorganylammonium salts can be used successfully to accelerate nucleophilic addition to the triple bond[187]:



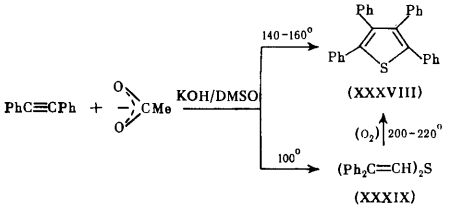
Catalyst	Dibenzo-18-crown-6	TEBA*	Without catalyst
yield of (XXXIII), %	72	37	0



Catalyst	Dibenzo-18-crown-6	TEBA	Without catalyst
Yield of (XXXIII), %	40	22	9

*Triethylbenzylammonium chloride.

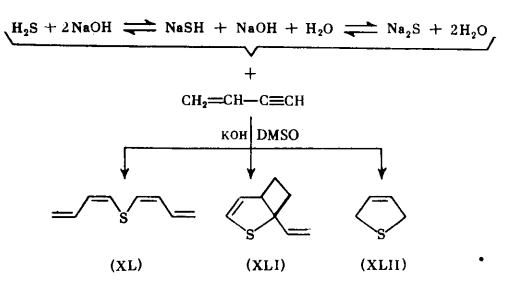
Depending on the conditions, either tetraphenylthiophen (XXXVIII) or di(2,2-diphenylvinyl) sulphide (XXXIX) can be obtained by the reaction of the thioacetate anion and diphenylacetylene[190]:



The "geminal" structure of the sulphide (XXXIX) is a result of an unexpected rearrangement with transfer of the phenyl group. The thermo-oxidative cyclisation of this sulphide to tetraphenylthiophen involves the reverse 1,2-migration of the phenyl groups[190]. A similar 1,2-migration is observed on heating the sulphide (XXXIX) with alkali in DMSO, which results in the reformation of diphenylacetylene[180,190].

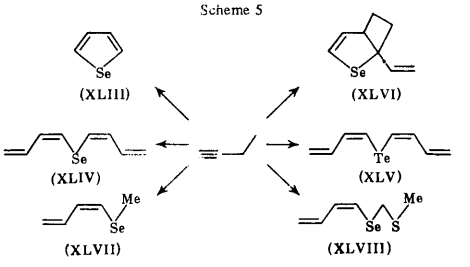
In conclusion of this section, it must be specially emphasised that almost all the reactions considered here are fairly general and are characteristic not only of acetylene itself but also of substituted acetylenes. For example, vinylacetylene reacts with sulphide anions in a superbasic medium to form di(buta-1,3-dienyl) sulphide (XL) [191] in a yield exceeding 90% (Scheme 4). By altering the conditions, it is possible to induce heterocyclisation reactions leading either to 1-vinyl-2-thiabicyclo[3,2,0]hept-3-ene (XLI) [192] or to dihydrothiophen (XLII),[193,194], which has been hitherto difficult to synthesise. The latter can be obtained in a virtually quantitative yield.

Scheme 4

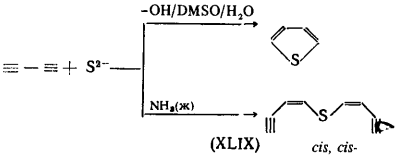


Direct single-stage syntheses (Scheme 5) of selenophen (XLIII), di(buta-1,3-dienyl) selenide (XLIV),[195] di(buta-1,3-dienyl) telluride (XLV),[195] 1-vinyl-2-selenabicyclo[3,2,0]-hept-3-ene (XLVI), as well as buta-1,3-dienyl methyl selenide (XLVII) [196] and buta-1,3-dienyl methylthiomethyl selenide (XLVIII), formed with participation of DMSO, have been achieved on the basis of vinylacetylene and the corresponding elements in superbasic media. The syntheses based on vinylacetylene and elemental selenium or tellurium in the KOH–HMP–H_2O and KOH–DMSO–H_2O systems at 100–120 °C are illustrated in Scheme 5 below:

Scheme 5



Sulphide anions react with diacetylene in superbasic media to give a quantitative yield of thiophen[197] or *cis,cis*-di(but-1-en-3-ynyl) sulphide (XLIX) in 89% yield[198]:



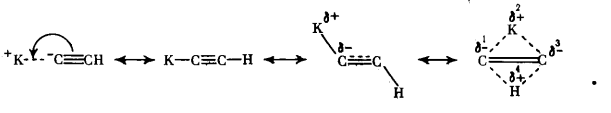
The last reaction has been achieved in liquid ammonia, which is also an effective superbasic medium, since it exhibits a high dielectric constant and an unsurpassed ability to solvate alkali metals, while its autoprotolysis constant is negligible.

VI. CONCLUSION

In conclusion one must say that, in order to avoid making the schemes and discussions unduly cumbersome, we excluded the ionisation of acetylene and the dissociation of acetylides:

$$HC\equiv CH + KOH \rightleftarrows {}^{+}K^{-}C\equiv CH + H_2O;$$
$${}^{+}K^{-}C\equiv CH \rightleftarrows K^{+} + {}^{-}C\equiv CH .$$

It would be a mistake to underestimate the influence of these reactions, particularly when one is dealing with superbasic media. Ideed, in the acetylide ion pair the triple bond, subjected to the influence of the charge and the electron cloud of the cationised alkali metal atom, should be very highly polarised and loosened:



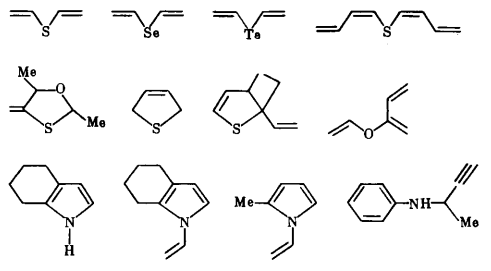
The extensive rehybridisation and stretching of the C≡C bond under the influence of the alkali metal attached to it directly is indicated particularly by the considerable decrease of the stretching vibration frequencies ν(C≡C) and ν(≡C–H) in the spectra of acetylides compared with alkylacetylenes[199]:

Acetylenic compound	$\nu_{C\equiv C}$, cm^{-1}	$\nu_{\equiv C-H}$, cm^{-1}
$CH_3C\equiv CH$	2121	3320
$LiC\equiv CH$	1990	3245
$NaC\equiv CH$		3216
$KC\equiv CH$		3224

One cannot rule out the possibility that the formation of acetylides makes a decisive contribution to the activation of acetylene by superbasic media. It may be that acetylene undergoes complex formation and is involved in key inner-sphere transformations precisely in the form of a polarised anion.

The review can be aptly concluded by listing the structures of the most readily available monomers, intermediates, and synthons (Scheme 6), which can now be readily obtained from acetylene in superbasic media and to which it is desirable to draw the attention of synthetic chemists, specialists in polymer chemistry, pharmacologists, biologists, and technologists.

Scheme 6



Thus a new stratum of fundamental and applied developments has arisen in acetylene chemistry. The possibilities of superbasic catalytic systems are by no means exhausted. The next development should be the creation of a rigorous quantitative theory, which would permit the specific employment of the above systems in practice as well as in further research.

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The Mechanism of the Electrophilic Addition of Halogens to a Multiple Bond

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A systematic account is given of the literature data on the mechanism of the electrophilic halogenation of olefins. Particular attention is devoted to the experimental methods for the investigation of the structures and reactivities of the intermediate unstable adducts produced by the electrophilic addition of the halogen to the multiple bond. The relation between the mechanisms of electrophilic halogenation and other *Ad* reactions is discussed. Certain aspects of the stereochemistry of the addition of halogens and hypohalites to olefins are examined.
The bibliography includes 192 references.

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I. INTRODUCTION

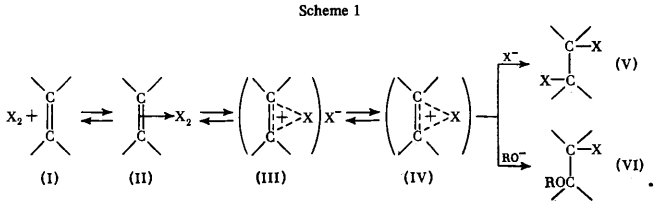
The electrophilic addition of halogens and hypohalites to olefins is a fairly well known reaction[1], but the study of its mechanism is still being continued[2-4]. The present review attempts to give a systematic and critical account of the available data (using studies published up to 1978), mainly from the standpoint of the reaction mechanism, the structure of the intermediates, and the influence of the structure of the reactants on the rate of their interaction. The synthetic aspects of the problem as well as the role of the donor–acceptor complexes are considered briefly, mainly in relation to new data which have not been included in recently published reviews[3-5].

II. THE REACTION MECHANISM. GENERAL KINETIC FEATURES

1. General Consideration of the Mechanism

The mechanisms of the halogenation and coupled halogenation of olefins (I) are closely related, as can be readily seen from Scheme 1 below:

Scheme 1



The first stage involves the formation of a π-complex (II) from the initial reactants, which is then converted into a "close" ion pair (III) (analogous to a σ-complex in aromatic substitution reactions); the latter then dissociates in media with a high solvating capacity into two solvated ions—the anion X^- and the cation (IV).[6-11]. In non-polar weakly solvating media the intermediate is a solvate-separated pair (IV) $\| X^-$.[6,12-14].

The rate-limiting stage of the entire process is ionisation of the π-complex (II) with formation of ion pairs[5,15,16]. Products (V) and (VI) are formed simultaneously, since the ratio of their yields is independent of the extent of reaction and remains constant[17,18]. Depending on specific conditions (the polarity of the medium, the structure of the components, and the reaction temperature), the proposed mechanism can be modified. The rate of formation of the final products depends not only on the rate of conversion of intermediates (III) or (IV) but also on their absolute concentrations. The rates of formation and decomposition of the unstable intermediates have not been determined directly but with the aid of low-temperature infrared, untraviolet, and ^1H NMR spectroscopy it has sometimes been possible to identify the intermediate[19,20] whose structure determines the mode of addition of the reactants and the stereochemistry of the final adducts[21].

On the other hand, during the last 15 years new facts have been observed, which can be regarded as evidence in support of the mechanism described in Scheme 1.

1. An anomaly in the temperature variation consists in the fact that k_{eff} for electrophilic addition either increases slightly[22-24] or actually decreases as the temperature rises[25-27], i.e. the effective activation energy is less than zero. This agrees well with the concept of the reversible formation of the intermediates (III) and (IV) with a considerable energy release. A negative temperature coefficient ($E_{act}^{eff} \leq 0$) was found initially only for chlorination[22] and bromination[27] reactions and was later noted for the addition of mixed halogens[28] and for coupled bromination or chlorination[26,29]. Since it is clear from Scheme 1 that $E_{act}^{eff} = \sum \Delta H + E$, where E is the activation energy for the conversion of (IV) or (III) into (V) and (VI) and $\sum \Delta H$ is the sum of the exothermic heats of the equilibrium stages, it follows that, when $\Delta H \ll 0$, the effective (or apparent) activation energy can become zero or even less than zero. Only one of the components is determined experimentally, namely the enthalpy of formation of the donor–acceptor complex (II), the absolute

value of which varies in the range 2–10 kcal mol^{-1} depending on the nature of the olefin and the halogen[5,30,31].

2. The halogenation of pure *cis*- or *trans*-isomers of olefins takes place stereospecifically. Thus it has been noted for *cis*- or *trans*-but-2-ene[32], d_3-styrene[33], and di-isopropylethylene[34] that the *anti*-addition of the halogen to the olefin takes place to the extent of 99.5%; this forced the investigators[32–34] to postulate that a cyclic halonium ion, with restricted rotation about the carbon bond, is involved exclusively in the reaction. Because of this, pure stereoisomers were isolated as a result of the reaction.

3. In the study of the behaviour of vicinal dihalogenoderivatives in strongly acid media, the ^1H NMR spectra demonstrated unambiguously the existence of intermediates whose interaction with methanol yields mixed adducts of type (VI), equivalent to products obtained in the coupled halogenation of an unsaturated compound in the presence of methanol[35].

It is seen from the evidence presented above that the structure of the intermediate determines the mode and rate of electrophilic addition to the double bond.

The existence of an equilibrium stage preceding the formation of adducts (V) and (VI) has been demonstrated most readily and convincingly with the aid of ultraviolet spectroscopy[30,31]. When equimolar amounts of bromine and cyclohexene are mixed, a 1:1 charge-transfer complex is formed and can be detected by the stopped flow method ($\lambda_{max} = 290$ nm; $\varepsilon \cong 15400$).[31] Similarly charge-transfer complexes have been identified in the chlorination of cyclohexene and hexene ($\lambda_{max} = 248$ and 263 nm; $\varepsilon \cong 1400$ in both cases).[30] The main difficulty arising in the study of the intermediate compound in olefin–halogen systems by ultraviolet spectroscopy arises from the fact that the σ- and π-complexes absorb in approximately the same spectral region; the initial molecules and electrophilic adducts as a rule also absorb in this region of the spectrum. It is therefore impossible to detect and identify the ultraviolet spectra of the separated and non-separated ion pairs whose concentration determines the mode and rate of electrophilic addition of the halogen.

The thermodynamic parameters of the reversible formation of charge-transfer complexes were found from the temperature variation of the equilibrium constants. The enthalpy of formation of the bromine–cyclohexene complex ($\Delta H \cong -4$ kcal mol^{-1}) [31] proved to be greater in absolute magnitude than for the chlorine complexes of hexene and cyclohexene ($\Delta H = -1.7$ and -2.7 kcal mol^{-1} respectively),[30] which indicates a lower stability of the olefin—chlorine complexes and is associated with a weaker polarisability of chlorine compared with bromine. The influence of the structure of the olefin on the thermodynamic parameters of the complex is related to the ionisation potential of the unsaturated compound (I) and the σ constants of the substituents[12,36]; the observed linear relations are described by the equations $h\nu_{eV} = 0.56I + 2.39$ and $\lg(k/k_0) = -3.16\sigma$.

The enthalpies of formation of the complexes obtained do not exceed 7.5 kcal mol^{-1} (for bromine iodide) and cannot explain the anomalous temperature variation of the rate constants for the electrophilic halogenation and coupled reactions, for which a negative temperature coefficient has been frequently observed[22,26,27,29,37]. It is logical to postulate the existence of at least yet another exothermic process[33,39] whose contribution would account for the decrease of the apparent activation energy to negative values. At the present time there is no unanimous view concerning the equilibrium which gives rise to the additional energy. A number of workers believe that the initially formed π-complexes rearrange to more closely linked "internal" complexes characterised by a higher degree of charge transfer[37]; the concept of the "internal" complex is apparently equivalent to the σ-complex and that of the "external" complex is equivalent to the π-complex.

Different exothermic processes are important for the mechanism of the electrophilic reaction: the formation of 2:1 halogen–olefin complexes[27,38] and the formation of complexes between the reactants and the solvents, including weakly polar solvents[39]. In polar solvents, particularly those which contain a heteroatom and are effective *n*-donors, the halogen forms a complex with the solvent. The enthalpy of formation of halogen–*n*-donor complexes is frequently higher[40] than that for olefin–halogen complexes. For example, $\Delta H = -8$ kcal mol^{-1} for the complex of epoxycyclohexane and bromine[41], which is twice as high as the enthalpy of formation of a complex between cyclohexene and bromine[31]. *n*-Donors are in fact most frequently involved in a coupled electrophilic reaction leading to the formation of mixed adducts, which have been established for α- and β-oxides[37,42–47], alcohols[48], and aliphatic[49–51] and acyclic[52,53] esters and anhydrides[54].

The reversible reaction between halogens and oxygen-containing *n*-donors can proceed via a two-well kinetic model[41,55] (like the interaction of a halogen with olefins) with conversion of the "external" complex formed initially into an "internal" complex[41]. The high exothermic heat of formation of complexes between *n*-donors and halogens is responsible for the occurrence of side reactions involving the isomerisation and polymerisation of the oxygen-containing donors; thus, depending on temperature and other conditions, in the case of an epoxide different amounts of dioxans and epoxide polymers were detected in the reaction mixture as well as the product of addition to the double bond[56].

Electrophilic halogenation begins with a series of reversible stages, including the formation of π- and σ-complexes. The problem therefore arises whether these two intermediate species, separated by a transition state with a low energy level, are in a state of equilibrium or whether their transformation is irreversible. The salt effect can serve as an indirect characteristic of the position of the equilibrium between intermediates (II) and (III). The addition of an electrolyte containing an anion common to the reactants increases the rate of conversion of the π- or σ-complex as a result of an increased concentration of the nucleophile attacking the intermediate; this phenomenon will be considered in detail below. The introduction of neutral electrolytes, without anions common to the reactants, into the electrophilic addition reaction will have an effect only in those cases where a solvate-separated ion pair (σ-complex) arises as an intermediate or individual ions are formed[57,58]. The positive salt effect is explained in this case by the fact that the electrolyte increases the degree of charge separation in the intermediate (III) and stabilises the latter as a result of association; the changes enumerated above lower the apparent activation energy for the entire electrophilic halogenation process. In the chlorination of *trans*-cinnamic acid the reaction rate constant increases by a factor of three in the presence of 0.1 M $LiClO_4$.[10]

The introduction of a neutral salt prevents the association of the separated ion pair into a non-separated pair (Scheme 1) and therefore displaces the equilibrium towards the more reactive σ-complex, so that the reaction rate constant increases. Added electrolyte increases the rate constant for the bromination of styrene by a factor of seven[57]. The increase in the degree of charge separation in the intermediate should increase the sensitivity of the halonium ion to the influence of substituents and the reaction rate constant should therefore increase in absolute magnitude. With

increase of the $LiClO_4$ concentration from 0 to 10^{-1} M in the acetoxy-bromination of R-styrene (Fig.1), the reaction rate constant increases owing to the increased dipole moment of the intermediate; the intersection of the two relations at the point corresponding to *m*-nitrostyrene can be explained only by the fact that the bromination involves the existence of only a solvate-separated ion pair whose state does not change with increase of the electrolyte concentration[57].

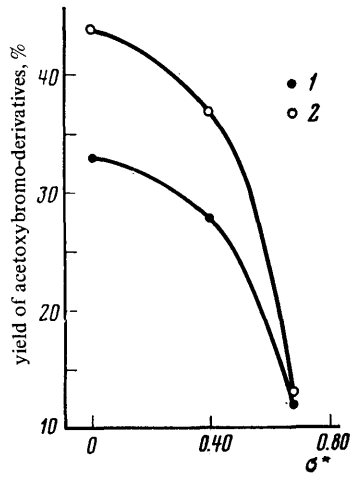


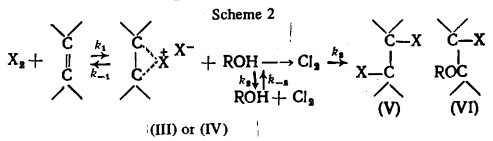
Figure 1. Dependence of the yield of the acetoxybromo-derivative in the bromination of R-styrene in acetic acid on the σ^+ constants of the substituents: *1*) acetic acid; *2*) acetic acid + 0.10 M $LiClO_4$.

2. The Ratio of the Rates of Individual Stages

Since the interaction of a halogen with an olefin proceeds at a high rate, it is frequently assumed that the electrophilic addition is irreversible. On the other hand, a number of facts are presented above confirming the formation of intermediates which are subsequently converted into the reaction products (V) or (VI). The entire reaction involving the electrophilic addition of a halogen to an olefin proceeds under pseudostationary conditions, so that the intermediates do not accumulate in large amounts. It is not possible to detect the intermediate species, because the rate of their formation is comparable to the rate of their conversion into the reaction products. The rate constant for the rate-limiting stage of a complex process involving the formation of products from an intermediate (III) or (IV) is close to the apparent rate constant for the entire process determined experimentally. The absolute value of k_{eff} varies within broad limits, depending on the structure of the olefin; thus k_{eff} varies in the range from 5×10^{-2} to 5×10^5 litre mol^{-1} s^{-1} in the bromination of *cis*- and *trans*-substituted olefins at 25 °C.[34,59]

In the coupled reaction the formation of a second donor–acceptor complex is no less important than the formation of the halogen–olefin σ-complex (Scheme 2):

Scheme 2



The exothermic heat of the two reversible processes lowers the effective activation energy for the electrophilic reaction. The addition of π- and *n*-donors not involved directly in the electrophilic addition reaction should have a catalytic effect owing to the formation of donor–acceptor complexes with the halogen. Thus, in the study of the electrophilic addition of chlorine to hexene in CCl_4, an increase of the rate constant and a change of the kinetic equation were observed in the presence of benzene or dioxan; on passing from CCl_4 to an electron-donating solvent, the rate constant changes from 1.7 litre mol^{-1} min^{-1} to 4800 $litre^2$ mol^{-2} min^{-1}.[60] Analogous results have been obtained also for other electron-donating solvents (diethyl and dibutyl ethers) which do not enter directly into the reaction under the experimental conditions[61].

However, a whole series of donors react with the halogen–olefin π-complex, forming mixed adducts[23,24,26,29,62]. The formation of donor–acceptor complexes of *n*-donors with chlorine has been indicated in kinetic studies by an increase in the reaction order with respect to the halogen in coupled reactions[23,24,63] and by the necessity for an excess of the oxygen-containing donor for the reaction to occur at a high rate. A decrease of the concentration of both chlorine and the *n*-donor inhibits the coupled reaction; in this case the kinetic curve acquires the S-shape characteristic of auto-catalytic reactions. The induction period of the auto-catalytic reaction is associated with the need to accumulate a considerable amount of the intermediate[64]. The presence of an induction period has been noted, for example, in the coupled bromination of cyclohexene in the presence of epoxycyclohexane[37].

With increase of temperature, the specific rate constants corresponding to the elementary stages of the process shown in Scheme 2 increase unequally; the dependence of the effective rate constant for the coupled halogenation on temperature is therefore anomalous—the absolute value of the effective rate constant decreases with increase of temperature[29,37]. Analysis of the process in Scheme 2 readily shows that an *n*-donor concentration higher than the stoichiometric value is necessary for the practical realisation of the coupled reaction. Reactions involving the coupled chlorination of allyl chloride together with α-oxides[29] and β-oxides[63] as well as 2-chloroethanol[24] take place in precisely this manner in the presence of an excess of the oxygen-containing compound.

If an appreciable charge separation takes place in the intermediate of the electrophilic reaction and the intermediate acquires the character of a solvate-separated ion pair, an increase in the concentration of the common halide ion should increase the rate of the electrophilic addition of the halogen to the multiple bond, i.e. a positive salt effect should be observed. Stimulation of the electrophilic bromination of olefins in methanol under the influence of NaBr has been most widely studied[65–67]. An increase of the concentration of the nucleophile increases (as a result of the dissociation of the electrolyte) not only the rate of the electrophilic reaction but also the fraction of *trans*-addition to the double bond. Nucleophilic attack on the carbon atom does not require in this case either a reorientation of the nucleophilic bromine or rotation about the carbon–carbon bond in the intermediate. With increase of the LiBr concentration in the bromination of styrene from 0 to 0.1 M, the fraction of *trans*-addition increases from 72 to 95%.[68]

The positive salt effect of the halide anion is described by a third-order kinetic equation incorporating the concentrations of both the halogen and the halide anion[69]. Electrophilic addition to an olefin in the presence of metal halides is a process which proceeds via two bimolecular collisions; the effective activation energy for this reaction is reduced,

since the energy expended on the dissociation of the halogen–halogen bond is compensated by the energy of formation of the halogen–carbon bond[70,71].

In those cases where the intermediate in the electrophilic addition of a halogen to a multiple bond acquires the character of a close ion pair (a π-complex) the addition of metal halides does not alter either the rate of reaction or the proportions of the *cis*- and *trans*-additions. In the chlorination of phenanthrene the addition of LiCl does not effect the stereochemistry of the halogen addition products[72]. An increase of the chloride ion concentration does not change the rate constants for the chlorination of *trans*-cinnamaldehyde[10] and *trans*-cinnamic acid[11]. In the study of salt effects it is important to take into account the formation of mixed adducts with protic solvents, since in this case hydrogen chloride is generated, increasing the rate of the electrophilic reaction by a factor of 10–12, which makes the addition of the halogen to the multiple bond autocatalytic[10,73].

The kinetic equation for the electrophilic addition of bromine to olefins is more complex: the reaction proceeds via two parallel competing pathways[58,59,74,75], involving the interaction of the olefin with molecular bromine (k_1) and with the tribromide anion (k_3); the latter interaction is described by the equation

$$Br_2 + Br^- \rightleftarrows Br_3^-$$

$$-\frac{d[Br_2]}{dt} = k_1\,[\text{olefin}]\,[Br_2] + k_3\,[\text{olefin}]\,[Br_3^-] \ .$$

The equilibrium constant for the formation of the tribromide anion has a high absolute value, so that minimal amounts of the common ion produced in the dissociation of the electrolyte shift the equilibrium towards the tribromide anion and reduce the contribution of the "molecular" reaction pathway. The equilibrium constant K_{25} depends on temperature, the source of the counterion, and the solvent. Thus, on passing from acetic acid to methanol, the equilibrium constant changes from 92 litre mol^{-1} (Rolston and Yates[57]) to 177 litre mol^{-1} (Dubois et al.[8]). The equilibrium constant changes even more when the nature of the electrolyte is altered; thus in the presence of HBr the equilibrium constant is 125 litre mol^{-1}, which is 2.5 times more than in the presence of added NaBr (53 litre mol^{-1}).[57,75] The equilibrium constant in the formation of the tribromide anion increases also with increase of the $LiClO_4$ concentration[57].

The relative contributions of the two parallel pathways are usually described by the ratio $Q = k_{Br_2}/k_{Br_3^-}$, which varies from 0.01 (Yates and Wright[58]) to 85 (Dubois et al.[8]). The change in the relative contributions of the competing pathways can be accounted for by the change in the bromide anion–tribromide anion equilibrium constant under the influence of the factors enumerated above. However, in all cases, ranging from dominant bromination by the tribromide anion ($Q < 1$) [58,74] to virtually complete absence of the reaction with the tribromide anion ($Q \gg 1$),[8,76–78] the rate of reaction of Br_3^- is higher than that of Br_2. The anomalously high values of Q observed by Dubois et al.[8] can be explained by the steric hindrance in the diphenylethylene being brominated and also by the autocatalytic effect of HBr, which is evolved on formation of mixed adducts with the solvent.

The interaction with the trichloride anion is less characteristic of chlorination owing to the low value of the equilibrium constant for the formation of the Cl_3^- anion[5,79,80]. On the whole, as in the cases enumerated above, the exothermic reversible formation of the trihalide ion exhibits a catalytic effect on the conversion of the intermediate into the reaction product; a change of temperature can alter the rate-limiting stage of the process, the rate constant for the reversible stage involving the formation of a π- or σ-complex being smallest.

III. PHYSICOCHEMICAL METHODS FOR DETECTING THE INTERMEDIATE SPECIES INVOLVED IN ELECTROPHILIC ADDITION REACTIONS

The electrophilic addition of a halogen usually takes place under pseudostationary conditions, so that the intermediate does not accumulate in considerable amounts, which hinders its detection by physicochemical methods. By carrying out the reaction at reduced temperatures, it is possible to separate the reversible and irreversible stages of the process (Scheme 1) and to investigate the structure of the unstable intermediates.

It has been shown[20,81–86] by low temperature infrared spectroscopy that, when an olefin and a halogen are sputtered onto a cooled (~–200 °C) cryostat support under molecular beam conditions, the spectrum shows initially only bands characteristic of the parent compounds. Heating of the cryostat support to between −180 °C and −165 °C leads to the mutual diffusion of the components and to the appearance in the infrared spectrum of a group of new bands which are not characteristic of either the initial compound or the reaction product[82,83,85].

The changes occurring in the infrared spectra can be explained solely by the formation of intermediates of the olefin–halogen type, which are converted on heating into dihalogeno-derivatives[81]. The decrease of the vibration frequency of the multiple bond suggests a decrease of its electron density compared with the initial olefin[83,84]. Analysis of the frequencies and modes of the normal vibrations shows that the olefin–halogen complexes have C_{2v} symmetry, which is characteristic of three-membered heterocycles[81]. Simultaneously with the structure, the equimolecular composition of the unstable intermediate was demonstrated[81–84]. In the presence of an excess of bromine an intermediate containing two bromine molecules per olefin molecule was detected[87]. In a mixture of bromine and propene the disproportionation of a 1 : 1 complex to give a 2 : 1 complex and free propene, identified in a mixture of complexes, was noted[84].

The conclusions reached in the study of the low-temperature spectra of halogen–olefin complexes were confirmed by quantum-mechanical calculations. The formation of the open-chain carbonium ion (VII)

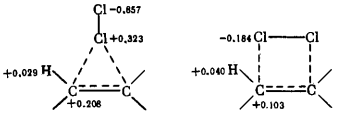


(VII)

incorporating an sp^3-hybridised carbon atom and a covalent carbon–carbon bond of normal length (1.53 Å), is unlikely; the existence of the carbonium ion is possible only when it is stabilised by the attacking nucleophiles[88,89]. Theoretically, the structure of the centrosymmetric halonium ion (IV) with a partially rehybridised carbon atom and altered valence angles is energetically most favourable[90,91]. The changes occurring on formation of intermediates can be followed in the infrared spectra of solid solutions of chlorine in olefins; the observed effects can be accounted for by a decrease of the electron density in the multiple bond and by the formation of partial C—Cl bonds.

For 1 : 1 donor–acceptor complexes of C_{2v} symmetry, two structures can be postulated[91,92]. The first is the axial structure (VIII) in which the halogen molecule is located on the symmetry axis of ethylene perpendicular to the carbon–carbon bond. In the alternative structure (IX) the halogen–halogen bond is parallel to the plane of the carbon–carbon bond. The complex (IX) presupposes the formation of a four-centre transition state and the *cis*-addition of a halogen

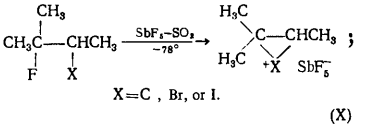
molecule to the multiple bond. Comparison of the distributions of electron density in the intermediates (VIII) and (IX) in the reaction involving chlorine shows that the former is energetically favoured, since it involves a greater charge separation[90].



(VIII) (IX)

According to quantum-mechanical calculations[90], the stability of the intermediate complexes decreases in the sequence Br > Cl > F, which agrees well with experiment[93]. The cyclic structure of the intermediate ion makes it possible to explain the *trans*-specificity of the electrophilic halogenation in non-polar media, associated with the inhibition of the free rotation about the carbon–carbon bond in the cyclic ion (VIII), compared with the open-chain carbonium ion (VII).[94,95] In polar media where there is a possibility of the formation of solvate-separated ion pairs, the open-chain ion may be stabilised† and the stereospecificity of the reaction may be infringed[96]; *cis*-addition to the multiple bond is possible only when there is rotation about the carbon–carbon bond in the intermediate. α-Substitution in the olefin molecule distorts the symmetrical distribution of electron density on the carbon atoms and in the limiting case such an intermediate may become open-chain[98–100]. Quantum-mechanical calculations have now been made only for the simplest olefins (ethylene and propene); the stabilising influence of the solvent on the charge distribution in halonium ions has been taken into account only indirectly[99]. The latter factor precludes an unambiguous utilisation of the quantum-chemical results for the consideration of the mechanism of electrophilic halogenation.

NMR has been widely used in recent years in the study of labile intermediates. A major achievement of NMR has been direct detection of non-classical cyclic halonium ions. Olah and coworkers frequently detected the formation of a cyclic intermediate from the corresponding vicinal dihalides when the latter were dissolved in superacids at low temperatures[35,93,101–108]. The dissolution of 3-chloro-, 3-bromo-, or 3-iodo-2-fluoro-2-methylbutane in an SbF_5–SO_2 mixture at −78 °C leads to the formation of the stable trimethylethylene–halonium ion (X):[104]

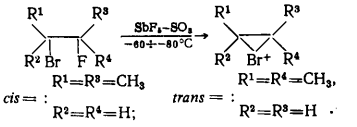


X=C , Br, or I.

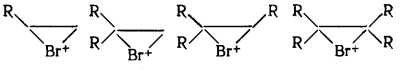
(X)

In the case of symmetrical ethylenehalonium ions[103,109] the conclusion that the ion had a bridged structure is based mainly on three pieces of evidence: the detection of a singlet signal due to the methylene protons in the ^1H NMR spectra, the upfield shift of the signal of the α-carbon atoms (to 40 ppm.) [105] relative to the spectra of typical open-chain ions[93], and the stereoselective methanolysis of the halonium ion generated from the optically active vicinal dihalides[93]. The presence of even insignificant amounts of a classical carbonium ion containing an sp^3-hybridised carbon atom should lead to the non-equivalence of the signals of the methylene protons and to the formation of racemates on solvolysis[102,103,162].

When *erythro*- and *threo*-3-fluoro-2-iodobutanes were ionised in superacids, the *trans*- and *cis*-iodonium ions were obtained, their reactions with CH_3OH proceeding stereospecifically with formation of *erythro*- and *threo*-*dl*-2-iodo-3-methoxybutanes respectively[35]. Indeed, if the non-classical halonium ions are three-membered cyclic species, they should have both *cis*- and *trans*-isomers. In a study of the low-temperature ^{13}C NMR spectrum of *erythro*-*dl*- and *threo*-*dl*-2-bromo-3-fluorobutanes in superacids both the *trans*-isomer ($\delta_{C_1} = \delta_{C_2} = 85.0$ ppm., $\delta_{CH_3} = 175.4$ ppm.) and the *cis*-isomer ($\delta_{C_1} = \delta_{C_2} = 82.9$ ppm., $\delta_{CH_3} = 174.4$ ppm.) of the dimethylethylenebromonium ion were identified[107]:



The introduction of alkyl substituents at the α-carbon atom stabilises the bridged ion; this has been demonstrated not only by NMR [103,107] but also by special thermochemical studies in superacids at −60 °C. The heat of formation of methyl-substituted bromonium ions varies in the following sequence[110]:

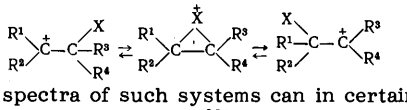


ΔH, kcal mol^{-1} −3.29 −8.39 −13.5 −22.5 .

The tetramethylbromonium ion proved to be the most stable, in agreement with conclusions which follow from spectroscopic studies[108]. The halonium ions of olefins substituted in the α-position by bulky alicyclic groups, for example, the adamantane ring, are particularly stable and can be isolated at the usual temperatures[111,112]. The structure of the adamantylbromonium ion has been confirmed mass-spectrometrically[111].

The substitution of the protons at the α-carbon atom of the olefin by arene rings leads to the destabilisation of the cyclic halonium ion and to the appearance of considerable amounts of an open-chain halonium ion; the presence of the latter has been demonstrated not only by NMR but also by the formation of a mixture of isomers in the solvolysis reaction[105,106].

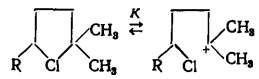
The stability of the cyclic ions increases in the following sequence of halogens: F < Cl < Br ≪ I,[107] which corresponds to the increase of the ionic radius and the polarisability of the atoms. The formation of a non-classical ion from fluorine is doubtful[113]. Bridged (butene[103] and ethylene[109]) and open-chain (propene[102]) ions are apparently characteristic of chlorine. It is logical to suppose that both forms under consideration are in a state of dynamic equilibrium:



The ^1H NMR spectra of such systems can in certain cases show a broadened singlet signal[114], which hinders its assignment to a specific type of ion. The problem can be solved using the temperature variation of the ^1H NMR spectra, which provides an unambiguous answer to the question whether or not a reversible reaction of the ions takes place in the given case. Such a temperature dependence has now

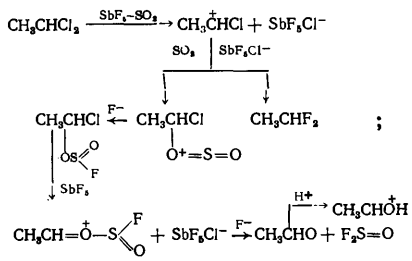
†According to quantum-mechanical calculations, the open-chain form $CH_3CH_2^+$ of the cation $C_2H_5^+$ is more stable than the cyclic form by 6.7 kcal mol^{-1}.[97]

been investigated only for the substituted tetramethylene-chloronium ion, whose stability is higher than that of the ethylenehalonium ion[115]. The predominance of the open-chain form of the ion over the cyclic form has been noted; the equilibrium constants K are 0.31 litre mol^{-1} in SO_2ClF and 0.21 litre mol^{-1} in SO_2.[115] An increase of temperature from −100° to −33 °C increases the content of the cyclic form from 10.5 to 25%:[115]



An increase of the size of the ring for the same number of methyl substituents in the α-position relative to the halogen atom greatly increases the stability of penta- and hexamethylenechloronium ions[116] compared with ethylenehalonium ions[110,117]. The available information about the trimethylenehalonium ion is contradictory[113,116]; the attempts to detect this ion proved unsuccessful owing to its rapid isomerisation to an ethylenehalonium ion[113]. In terms of their reactivities, the five- and six-membered halonium ions are analogous to ethylenehalonium ions[76,115,118–120].

The data concerning the formation of non-classical bridged ions, obtained with the aid of low-temperature NMR, cannot be transfered mechanically to the consideration of different aspects of electrophilic reactions, since highly ionising media (SbF_5–SO_2 and SO_2ClF–SO_2) and a low temperature have a stabilising influence on the unstable intermediates. The conversion of the latter on heating does not always proceed solely with the electrophilic addition of the halogen to the multiple bond, with formation of an adduct, but can be complicated by a whole series of side reactions. An example of degradative decomposition is provided by the conversion of the cation obtained from 1,1-dichloroethane in the SbF_5–SO_2 medium[35]; in this case only the products of the conversion of the initially formed ion were identified in the reaction mixture[35]:

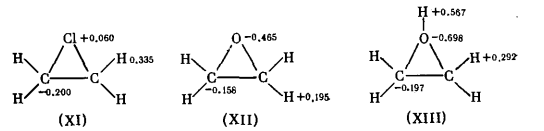


The formation of the ethylenechloronium ion in SO_2ClF is complicated by the 1,2-hydride shift[109].

Overall, the study of the NMR spectra of dihalides at low temperatures confirms the validity of the concept of cyclic halonium ions, because *cis–trans*-isomerism has been observed, the solvolysis proceeds stereoselectively, and the absolute values of the chemical shifts are not characteristic of classical carbonium ions.

IV. THE *Ad* MECHANISM OF THE ADDITION OF A HALOGEN TO A MULTIPLE BOND

If it is assumed that a bridged non-classical ion is involved in the electrophilic addition of a halogen to a multiple bond in non-polar media, then the conversion of the ion into products is a typical *Ad* reaction[18,121], the kinetics of which are common to other analogous reactions, for example, those involving the opening of the ring in epoxides under the influence of nucleophiles[122]. The principal objection to the proposed analogy is the nature of the distribution of electron density in the "bridged" ion (XI)—the intermediate in the electrophilic reaction[97]—and in the epoxide (XII):[123]



(XI) (XII) (XIII)

Systematic study of the quantitative characteristics of the opening of the epoxide ring under the influence of nucleophiles showed that the species which usually reacts is the protonated epoxide (XIII),[123,124] where the distribution of electron density differs significantly from that known for the epoxide (XII). The reactions of epoxides with nucleophiles under the conditions of both acid[125–129] and base[130,131] catalysis proceed via a trimolecular transition state incorporating both the nucleophile and the proton donor molecule. Protonation of epoxides increases the polarisation of the C–O bond, which facilitates its dissociation; the nature of the distribution of electron density in the intermediates (XI) and (XIII), formed respectively in the electrophilic addition of the halogen and in the opening of an epoxide, is the same, as has been frequently confirmed by quantum-mechanical calculations[98,123].

The chemical shifts (δ, ppm.) of the protons of protonated epoxides and certain halonium ions[132].

Ion	δ_{CH}	δ_{CH_2}	δ_{CH_3}
$CH_2(I^+)-CH_2$	—	5.77	—
$CH_2(Br^+)-CH_2$	—	5.53	—
$CH_2(OH^+)-CH_2$	—	5.00	—
$CH_2(SH^+)-CH_2$	—	3.63	—
$CH_3CH(I^+)-CH_2$	7.73	5.77	3.32
$CH_3CH(Br^+)-CH_2$	7.48	5.86	2.98
$CH_3CH(OH^+)-CH_2$	5.80	5.20	1.53
$CH_3CH(SH^+)-CH_2$	4.40	3.66	1.63
$(CH_3)_2C(I^+)-CH_2$	—	5.72	3.43
$(CH_3)_2C(Br^+)-CH_2$	—	5.55	3.32
$(CH_3)_2C(OH^+)-CH_2$	—	5.20	1.63

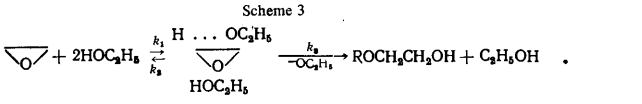
The genetic relation between the intermediates in reactions proceeding via the *Ad* mechanism has been demonstrated experimentally; Olan and Szilagy[132] established that the chemical shifts of the protons of the methylene groups in protonated epoxides and thiirans are similar to those of the cyclic halonium ions (see Table). It is easy to see that the change in the electronegativity of the heteroatom required

an increase of the chemical shifts of the methylene protons giving the following sequence: O > Br > S ≅ C > I.[133] The breakdown of this sequence can be accounted by the different directions of the shifts of electron density in the three-membered heterocycle: if the electronegativity of the heteroatom (Br, Cl, O) is greater than that of carbon, the electron shifts to a centre of the antibonding type (the carbon atom); if the heteroatom is less electronegative than carbon, the electron density of the carbon–heteroatom bond shifts in the opposite direction[99]. A second factor which distorts the sequence of the changes in the chemical shifts arising from the electronegativity series of heteroatoms, is protonation of the heteroatom.

The isotypical distribution of electron density in three-membered protonated heterocycles and in cyclic halonium ions, presupposes a close relationship between the mechanisms of the electrophilic halogenation and the opening of the epoxide rings under the influence of nucleophiles, which is shown particularly clearly in relation to coupled electrophilic reactions.

The π- or σ-complex formed in the first stage of the electrophilic addition is converted into an ether under the influence of the alcohol anion (Scheme 1);[23,24] the protonation of the epoxide under the influence of an alkoxide[124,130] or a phenoxide[126] (Scheme 3) proceeds in exactly the same way:

Scheme 3



The involvement in the transition state of the opening of the epoxide rings of at least two molecules—one proton donor molecule and one nucleophile molecule—has been confirmed by the high kinetic orders of the reactions of epoxides with phenols[126,134] and alcohols[125,135]. The high kinetic orders observed for the electrophilic addition of a halogen to an olefin ($n = 3$) [14,136] and for the coupled reaction[23,24,26] ($n \geq 3$) presuppose the formation of a trimolecular transition state via two bimolecular processes.

The identical characteristics of the charge distribution in the unstable intermediate adducts suggest the identical influence of the ionic strength of the solution on the rates of the two reactions. A positive salt effect has been noted for the opening of the epoxyethane ring under the conditions of acid catalysis[128] for the electrophilic addition of chlorine[71] or bromine[51] to a multiple bond.

The energy profiles of the reactions compared (Fig. 2) are identical[5,7,13], which permits the conclusion that the formation of the unstable oxiran–catalyst (or alcohol) adduct[124,131] is equivalent, from the standpoint of thermodynamics, to the formation of a σ- or π-complex in electrophilic halogenation. The exothermicity of the pre-reaction donor–acceptor interaction lowers the experimental apparent activation energy.

A decrease of the concentration of one of the initial reactants (Schemes 1, 2, and 3) or an increase of temperature leads to a shift of the pre-reaction equilibrium towards the initial reactants in accordance with the Le Chatelier principle, which lowers the concentration of the intermediate and the rate of the process as a whole. The inhibition of the reaction leads to the S-shape of the kinetic relation characteristic of an autocatalytic reaction[137]. Such relations, with an induction period, have been found for the reactions of epoxides with alcohols[130] and for coupled reactions[37].

The formation of cyclic halonium ions in electrophilic halogenation reactions in non-polar media inhibits the rotation about the carbon–carbon bond and increases the percentage of the *trans*-addition to the multiple bond[32,68]. In substituted epoxides, where rotation about the C–C bond is impossible, the probability of the *trans*-opening of the epoxide ring reaches 100%.[129]

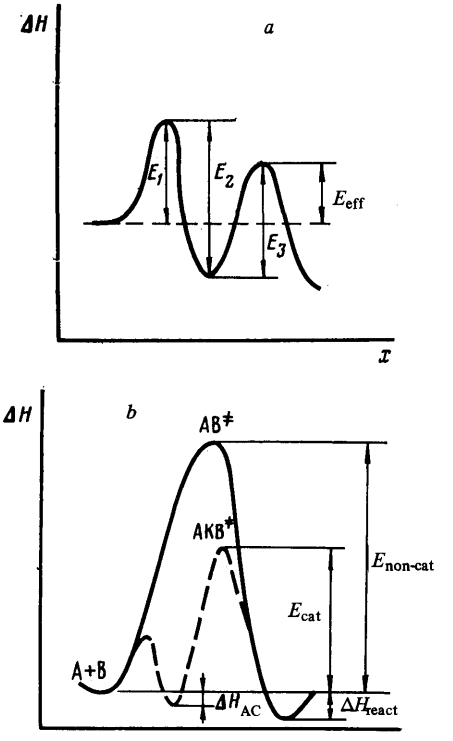


Figure 2. Variation of the potential energy along the reaction coordinate x: *a*) for the coupled halogenation of olefins:

olefin + halogen ⇄ olefin.halogen → mixed adducts / dihalogeno-derivatives;

b) for non-catalytic and homogeneous-catalytic reactions of an epoxide with alcohols:

epoxide + alcohol $\xrightarrow{\text{catalyst}}$ epoxide.alcohol.catalyst → products.
(A) (B)

V. STEREOCHEMICAL ASPECTS OF ELECTROPHILIC HALOGENATION

1. The Influence of the Structure of the Halonium Ion on the Stereochemistry of Electrophilic Halogenation

The study of the stereochemistry of the addition of halogens and hypohalites yields important information about the structure of the intermediate, the degree of ionisation, and the symmetry of the distribution of electron density between carbon atoms. In those cases where the intermediate is a typical halonium ion, the electrophilic reaction proceeds stereoselectively with the formation only of the products of *trans*-addition to the multiple bond[138]. The chlorination of butenes[21,95] and the bromination of ethylenes[21,34] can serve as examples of the stereoselective *trans*-addition.

The addition of mixed reagents, for example bromo- and chloro-acetoxylation, proceeds stereoselectively[34,139]. The stability of a cyclic halonium ion increases with increased atomic radius of the halogen; the stereoselectivity of the addition of a halogen to allyl ethers increases in precisely this sequence[21].

The increase of the degree of charge separation in the intermediate, due to external factors such as the polarity of the solvent[69,140] and the addition of salts[10], increases the probability of the formation of an "open-chain" ion and the stereoselectivity of the electrophilic addition of the halogen is then limited. An increase of solvent polarity in the bromination of *cis*-β-methylstyrene in the series from carbon tetrachloride to nitrobenzene reduces the percentage *trans*-addition from 70 to 45%; for *trans*-β-methylstyrenes, the effect of the change in solvent polarity is less pronounced (71% *trans*-addition for dioxan and 82% for nitrobenzene).[68]

The positive salt effect observed in the electrophilic addition of a halogen was discussed above[57]; the addition of an electrolyte alters not only the reaction rate constant but also the stereoselectivity of the process. The ability of the salt to stabilise the solvate-separated ion pair as a result of electrostatic interaction increases the probability of rotation about the carbon–carbon bond and infringes the stereospecificity of the electrophilic addition of a halogen to a multiple bond. In the chlorination of acrylic acid derivatives the yield of the *trans*-addition product is reduced by 30–35% in the presence of added $LiClO_4$.[9-11] In those cases where the electrophilic addition of a halogen in non-polar media proceeds with participation of a close ion pair, the influence of added electrolytes on the stereochemistry of the addition reaction should be minimal[32,68].

The comparatively simple postulates explaining the proportions of the *cis*- and *trans*-addition of a halogen to a multiple bond are distorted when the molecular reaction pathway is accompanied by a significant contribution by the radical non-stereospecific pathway[141], which is especially characteristic of reactions involving chlorine[142,143]. In the chlorination of *trans*-but-2-enes the contribution of the radical reaction increases as the olefin concentration is reduced and the number of alkyl substituents in the olefin is decreased[94]. The probability of the radical reaction changes in the sequence which is the opposite of that based on the stabilities of cyclic halonium ions (Cl > Br > I); for the addition of bromine to a multiple bond, the contribution of the free-radical reaction pathway is small[144].

In connection with the difficulty of determining the angle of rotation in the intermediate, which is rapidly converted into the reaction products, the stereochemistry of the electrophilic addition of a halogen to the multiple bonds of acyclic compounds, where rotation in the intermediate labile complex is impossible, acquires particular importance[72,145]. The interaction of chlorine with unsubstituted cyclohexene proceeds stereoselectively[72], while the addition of chlorine to acenaphthylene and phenanthrene results in a mixture of stereoisomers[72]. The absence of a definite stereospecificity for the electrophilic addition of chlorine to a multiple bond can be explained by the contribution of a free-radical process, which has been confirmed by the detection in the reaction mass of different amounts of radical-substitution products[145,146]. The principle, according to which an increase of the reactivity of the reagent reduces the selectivity of the reaction, holds for the electrophilic addition of a halogen to unsaturated acyclic compounds[147].

The high absolute rates preclude at the present time the estimation of the relative rates of rotation in the open-chain ion and of the addition of a halogen to the intermediate cation, but it is possible to estimate the thermodynamic parameters of these two processes. The thermodynamic parameters of the electrophilic reaction involving the geometrical isomers of olefins have been compared[57,68,148,149] with the enthalpies of their *cis*–*trans* isomerisation, estimated as differences between the heats of combustion of the *cis*- and *trans*-isomers. It is postulated[148] that, when the activated complex resembles an "open-chain" ion, the interaction of bulky alkyl substituents at the sp^3- and sp^2-hybridised atoms of the intermediate will be weakened as a result of the rotation; the difference between the enthalpies of the electrophilic halogenation of *cis*- and *trans*-isomers will then decrease relative to the enthalpies of isomerisation of the same geometrical isomers. In those cases where the activated complex has the structure of a halonium ion the steric influence of the bulky substituents is more pronounced; the difference between the enthalpies of the electrophilic addition reactions involving geometrical isomers therefore increases compared with the enthalpy of their isomerisation. The energy profiles of the bromination reactions of *cis*- and *trans*-stilbenes (Fig.3) show that the enthalpy difference in the transition state is greater than in the initial state, which corresponds to a cyclic bromonium ion and not an open-chain ion[148].

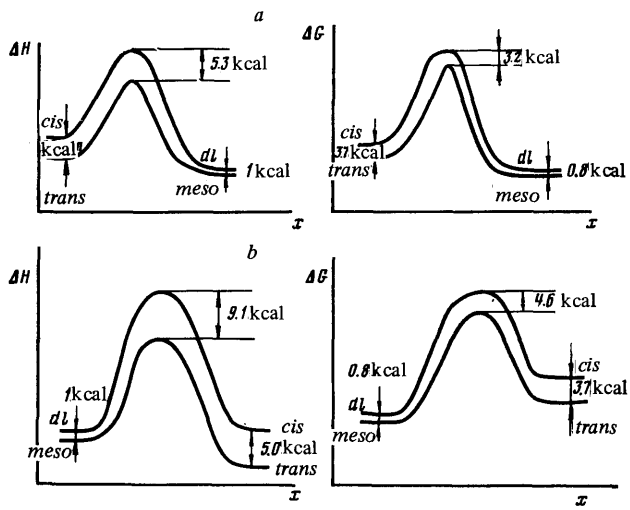


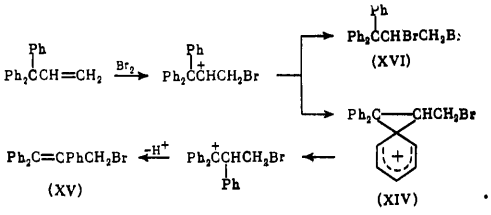
Figure 3. Variation of the enthalpy and free energy along the reaction coordinate for the bromination of *cis*- and *trans*-stilbenes in acetic acid[148] (*a*) and for the debromination of *dl*- and *meso*-stilbene dibromides in dimethylformamide catalysed by lithium bromide[151] (*b*).

Examination of the nature of the variation of the enthalpy along the reaction coordinate explains the higher rate constant for the electrophilic reaction involving the *trans*-olefins than for the *cis*-olefins, usually observed, since the potential barrier to the latter reaction is greater (Fig.3*a*) than the barrier to the former[69,138,150]. The difference between the energetic parameters of the electrophilic addition reaction agrees satisfactorily with the difference between the enthalpies of the debromination of the *dl*- and *meso*-dibromo-derivatives in dimethylformamide (Fig.3*b*) which apparently also proceeds via a stage involving the formation of a bromonium ion[151–153].

The joint study of the thermochemistry, kinetics, and stereochemistry of the addition of a halogen to the *cis*- and *trans*-isomers of an olefin yields the most complete information about the structure of the intermediate species.

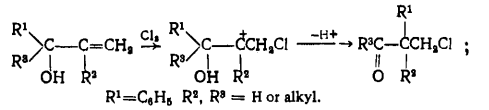
2. The Effect of the Involvement of Neighbouring Groups

The introduction of several substituents at one carbon atom alters the charge distribution in the intermediate[154], infringes the additivity of the influence of the substituents[155-158], and causes additional stabilisation of the charge on the cationic centre[159,160] due to interaction with the electron-donating groups located at the α-atoms of the carbon chain, which permits the migration of one of the substituents to an unsubstituted carbon atom of the olefin[161,162]. A characteristic example of the rearrangement of the carbon skeleton is the migration of the arene ring on bromination of 3,3,3-triphenylpropene[161]:



The presence of unduly bulky substituents at the carbon atom in 3,3,3-triphenylpropene, together with the stabilisation of the charge on the intermediate cation in the reaction with bromine, permits a direct interaction of the carbonium centre with one of the benzene rings. The intermediate phenonium ion has much in common with halonium ions; thus, when the reaction is carried out in methanol, a mixed adduct, incorporating the solvent, is obtained, apart from the rearrangement of product (XV) and the dibromide (XVI), as in other electrophilic reactions[161]. The bromination of 4-allylanisole leads to the formation of a mixture of a dibromide and a rearranged product, which are formed via two parallel pathways with participation of the bromonium and phenonium ions respectively[163]. The substitution of the benzene rings in 3,3,3-triphenylpropene with methyl groups increases the steric hindrance and makes the addition of a second bromine atom to the double bond more difficult; only the rearranged product is isolated from the reaction mixture in this case[161].

The reaction of olefins containing alkyl substituents proceeds in a more complex and more ambiguous manner[162, 164,165]. The reactions of alkenylalkylphenylmethanols with halogens and hypohalites have been studied in greatest detail[166-168]:

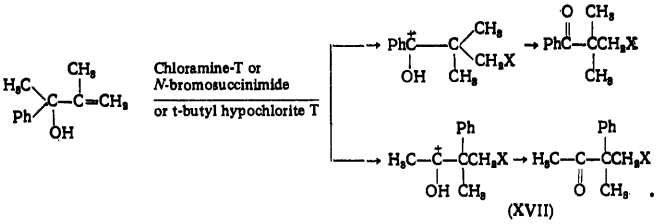


$R^1 = C_6H_5$; R^2, R^3 = H or alkyl.

In the case of acyclic compounds the rearrangement of the carbon skeleton proceeds with ring expansion[169,170]. Thus, for triphenylethylenes[161] in methanol, not only rearranged products and dihalides but also mixed products incorporating the solvent are formed[164,171,172].

The probability of the rearrangement of the halonium ions increases in the sequence Cl << Br < I;[173] the degree of stabilisation of the intermediates in the electrophilic addition reaction increases in precisely the opposite sequence[107].

The degree of delocalisation of the positive charge of the carbonium centre can increase under the influence of electron-donating substituents introduced into the migrating ring, which increases the rate of rearrangement[174]. In order to compare the stabilities of the phenonium, chloronium, and bromonium ions, Kartashov and Bodrikov[173] investigated the rearrangement of isopropenylmethylphenylmethanol under the influence of different agents:



(XVII)

A change in the nature of the halogenating agent does not alter the ratio of the reaction products: in all cases the ketone (XVII)—the product of the migration of the phenyl group—predominates, i.e. the interaction of the positively charged carbonium ion with the aromatic ring is more effective than the interaction with the unshared electron pair of the halogen atom; thus the phenonium ion is more stable than the chloronium or bromonium ion[173].

With decrease of solvent polarity as a result of the destabilisation of the positive charge in the intermediate, the rate of rearrangement increases[175]. Special experiments have shown that the competing reactions—rearrangement, substitution, or addition—are parallel pathways leading to the conversion of the intermediate halonium and phenonium ions[163,176] and that the thermodynamic parameters (enthalpy and entropy) of the rearrangement of the carbon skeleton[177] are similar to those usually observed for the electrophilic halogenation of olefins[178].

VI. THE ELECTROPHILIC PROPERTIES OF THE REACTION CENTRES OF THE INTERMEDIATE

The mode of addition of anions to the halonium ion arising in the intermediate stage of an electrophilic kinetically controlled reaction is determined by the relative electrophilicity of each atom of the intermediate. The reactivity of the latter depends on the basicity and polarisability of each carbon atom of the unstable intermediate and on the electronic nature of the substituents in the α-position relative to the multiple bond[4]. It is impossible to determine independently the basicities and polarisabilities of each reaction centre, because the two atoms are linked into a mesomeric system. The lack of quantitative characteristics necessitates the use of qualitative estimates for each electrophilic atom of the intermediate; Pearson's principle of hard and soft acids and bases (HSAB) [179-183] is most convenient for this purpose. Pearson's empirical principle has been explained on the basis of the quantum theory, where its fundamental concepts (softness and hardness) are related to the different energies of the highest occupied and lowest vacant orbitals[184].

The application of the HSAB principle is particularly effective when the relative amounts of the isomeric products of electrophilic addition to a multiple bond are considered. With increase of the number of methyl substituents at the carbon atom in the series ethylene, propene, isobutene[144,185], the hardness of the cationoid centre increases with a simultaneous increase of the amount of the mixed adduct involving methanol, because the latter is a harder reagent

than the bromide anion. The relative amount of the bromomethoxyalkane varies as a function of the degree of substitution, increasing from 38% for ethylene to 84.7% for isobutene[185]. The degree of formation of mixed adducts increases similarly in the chlorination of olefins in acetic acid[181] and methanol[187].

The addition of the elements of a hypohalite to allyl chloride can also be explained on the basis of the HSAB principle: the hardest reagent (the alkoxide anion) is coordinated to the hardest central atom of the allyl chloride molecule[188-191]. The study of the products of the addition of chlorine and acetate to allyl chloride and hexane showed that the amount of adducts formed in accordance with the Markovnikov rule decreases from 77.5 to 67%, which reflects the increase in the hardness of the carbon atom in the allyl chloride molecule[18].

Pearson's principle can be applied no less successfully when the influence of the solvent is considered; when solvent polarity varies in the sequence carbon tetrachloride < methylene chloride < methanol, the degree of charge separation in the intermediate increases and hence there is an increase in the tendency towards reactions with the harder reagent—an alcohol[190], an acid[17,95], an epoxide[188,189], or a β-oxide[63] rather than a halide anion.

The joint influence of several factors varying simultaneously is more difficult to interpret on the basis of the HSAB principle; thus, when the methyl group of propene is substituted by the benzene ring, the polarisability and hence softness of the carbon atom increase. Nevertheless, in polar media such as acetic acid[95,139,192] and alcohols[122,185] the preferential coordination of the α-phenyl-substituted atom of 1-phenylprop-1-ene to the hard base is observed and mixed adducts are formed; this can be explained by the considerable charge separation in the intermediate under the influence of the polar solvent, which increases the hardness of the system as a whole.

In all cases examined above the factors increasing the hardness and reducing the polarisability of the intermediate lead to the formation of mixed adducts in the electrophilic reaction rather than dihalides.

On the whole, one can conclude that the pre-reaction equilibrium stage in the addition of a halogen to a multiple bond is characteristic of all electrophilic halogenation processes without exception. The structure of the intermediates in the electrophilic halogenation reaction requires further refinement. The low-temperature infrared and NMR spectroscopic methods are the most promising for the solution of this problem. Another important task in the study of the mechanism of the electrophilic reaction is estimation of the partial constants for the multistage process. A detailed investigation of the mechanisms of the electrophilic addition of a halogen to a multiple bond is undoubtedly important for the development of ideas concerning electrophilic reactions.

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The Formation of the Azoxy-group in the Oxidation of Compounds with Nitrogen-Nitrogen Bonds

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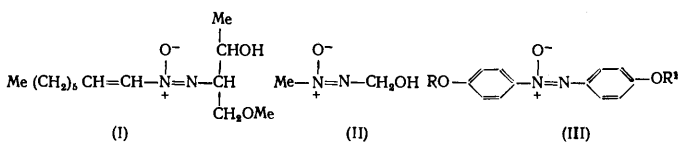
Methods for the formation of the azoxy-group by the oxidation of compounds with nitrogen-nitrogen bonds, namely azo- and hydrazo-compounds, indazoles, and hydrazones, are considered.
The bibliography includes 352 references.

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I. INTRODUCTION

The first example of azoxy-compounds, namely azoxybenzene, was obtained by Zinin in 1845.[1] During the succeeding century only episodic interest was shown in these compounds. The vigorous development of studies on such compounds was stimulated by the presence of the azoxy-group in certain natural products [macrozamin[2-4], elaiomycin (I),[5,6] cycasin[7-17], and LL-BH872α [18-20]] exhibiting a powerful pharmacological activity. It was found that the incorporation in food of the fruit of certain species of the coconut palm can give rise to cancer[7-17], the active principle being methylazoxymethanol (II) substituted in the hydroxy-group by a glycosidic residue[7-17]:



(I) (II) (III)

Methylazoxymethanol proved to be a powerful carcinogen, teratogen, and mutagen[7-17,21-24], the mechanism of the action of which is attributed to the alkylation of the amino-groups in DNA.[12-17,21-24] Many azoxy-compounds are now known to possess a powerful pharmacological activity[2-48] and the ability of the azoxy-group to induce mutations at a cellular level is used in preparations with tuberculostatic [compound (I)] and fungicidal activities[5,6,18-20]. It is remarkable that chemists were for a long time unable to establish the position of the *N*-oxide oxygen atom in compound (II); it was isolated for the first time as late as 1965 by the enzymatic hydrolysis of cycasin[21].

Another important stimulus of the development of the chemistry of azoxy-compounds was the discovery among azoxyarenes (II) of substances with liquid-crystal properties, exhibiting a positive dielectric anisotropy. In terms of thermal stability and a wide range of the existence of the mesophase, they are superior to many other substances of this type[49,50] and are therefore used in optical instruments, as phases in gas–liquid chromatography (GLC), and also in structural assignments with the aid of NMR and EPR.[49-59]

Finally, the chemistry of azoxy-compounds is of interest in view of the practical applications of pesticides, medicinal preparations, and dyes, whose structures include nitrogen-containing functional groups. The study of ways of converting these groups and the elucidation of the role of azoxy-compounds in the nitrogen turnover constitute an important fundamental task. As a result of the high thermal and chemical stabilities of the azoxy-group, azoxy-compounds serve, together with molecular nitrogen, as "trapping agents" in various changes of the valence state of nitrogen. Azoxy-compounds can be readily obtained from virtually any nitrogen-containing group by oxidation or reduction (including biochemical processes), but the reverse transformations are few and the synthetic value of the azoxy-group is not great.

Familiar monographs[60-67] contain chapters devoted to the azoxy-group. The early studies of the Italian and German schools on azoxyarenes were summarised by Angeli[68] and Bigelow[69]. The individual properties of the azoxy-group—photochemical reactions[70,71] and the Wallach rearrangement[71-73]—have also been considered. The properties of this group are described most fully in Patai's monograph[74] (see also the relevant reviews[75,76]).

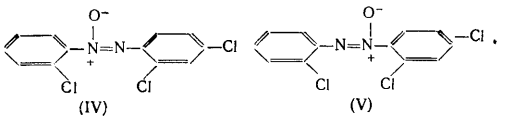
In the present review we shall consider methods for the synthesis of the azoxy-group by the oxidation of compounds with a nitrogen–nitrogen bond. Studies published up to the end of 1979 are discussed.

II. THE NOMENCLATURE OF AZOXY-COMPOUNDS

Publications on the nomenclature of azoxy-compounds[63,67,69] show that there is no unanimous point of view on this problem. The general name "azoxy-" for the group $-N=N^{+}-$ (with O^{-}) is used most frequently. If the group is linked to two identical substituents, the old nomenclature, in which the prefix "azoxy-" is placed before the name of the corresponding hydrocarbon [for example, azoxybenzene for $C_6H_5N=N(O)C_6H_5$] is entirely suitable. In the case of an asymmetric substitution at the $-N=N(O)-$ group the IUPAC nomenclature recommends the prefixes *–ONN–* or *–NNO–* to define the position of the oxygen atom[63,67,77]. When the atoms are arranged in the sequence *–ONN–*, the position of the substituent at the group linked directly to the

$\overset{+}{N}-O^-$ fragment is designated by a prime or, in the case of the reverse formulation of the azoxy-group (*–NNO–*), the prime denotes the position of the substituent at the group not linked to the NO fragment.

For example, in this nomenclature compound (IV) is called 2,2′,4-trichloro-*ONN*-azoxybenzene and compound (V) is 2,2′,4-trichloro-*NNO*-azoxybenzene:



(IV) (V)

Owing to their inconvenience and ambiguity, the IUPAC rules have not found extensive applications in complex cases.

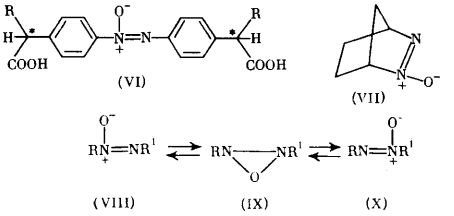
After the publication of the review of Spence et al.[70], the terminology employed by them began to be actively employed. Thus substituents in an aromatic ring linked to the $\overset{+}{N}-O^-$ fragment are given primed numbers and substance (IV), for example, is called 2,2′,4-trichloroazoxybenzene. At the same time a system of alphabetical designations is introduced. α-Compounds is the name given to isomers in which the $\overset{+}{N}-O^-$ fragment is linked to the smaller (phenyl relative to naphthyl) or less substituted aryl. These rules constitute a slight modification of the system of alphabetical designations introduced by Angeli (for examples, see Refs. 61, 62, and 69). At the same time, a nomenclature in which azoxy-compounds are designated as substituted diazene *N*-oxides[78] or di-imide *N*-oxides[79], has been used. The Chemical Abstracts Nomenclature (introduced from Volume 76) is the most promising, unambiguous, and consistent with the nomenclature of other functional groups (–N = N–, –N(O) = N(O)–, $>\overset{+}{N} = N^-$, etc.]. It is based on the name diazene oxide in which numerals 1 and 2 denote the positions of the substituents and the oxygen atom. However, this system is very cumbersome.

The terminology introduced by Moss and Love[80], in which the group linked to the $\overset{+}{N}-O^-$ fragment is designated as proximal and the group remote from the fragment is designated as distal, is suitable for asymmetrically substituted azoxy-compounds. Similarly, the position of oxygen at the nitrogen atom, adjoining the group Z in XN = N(O)–Z, is designated as proximal in relation to Z and the opposite position is designated as distal.

III. ISOMERISM OF THE AZOXY-GROUP AND STRUCTURAL ASSIGNMENTS

Several types of isomerism are possible for azoxy-compounds: the azoxy-compounds–oxadiaziridine valence isomerism, the *cis-trans* isomerism, and the isomerism based on the position of the oxygen atom at the nitrogen atom.

The azoxy-compound–oxadiaziridine isomerism is a special case of the ring–chain valence isomerism in a triad system; the total number of combinations of the CNO atoms has been examined by Greene and Hecht[81]. The asymmetry of the azoxy-group was first demonstrated by Angeli by chemical methods and was later confirmed by physicochemical studies[61–67,72]. Final evidence was provided by the resolution into optical isomers of the *trans*-azoxy-compound (VI, R = Et),[82] formed when the *meso*-azo-compound is oxidised, by the formation of the racemate and the optically active compound (VI, R = Me),[83] and by the asymmetric synthesis of the *cis*-azoxy-compound (VII)[84]:



(VI) (VII)

(VIII) (IX) (X)

After the asymmetry of the azoxy-group as well as the erroneous nature of certain reports of the isolation of oxadiaziridines had been firmly demonstrated, much effort was devoted to the synthesis of this cyclic form.

Numerous attempts to detect 2,3-diaryloxadiaziridines (IX, R,R^1 = aryl) proved fruitless. Neither treatment of azoxy-compounds with strong acids[71,72,85], nor their irradiation[71,86–94,97,98], nor the oxidation of *trans*- or *cis*-azoarenes[95–97], nor other reactions[87] yielded the three-membered ring. However, these negative results did not resolve finally the problem of whether or not the migration of oxygen from $N_{(1)}$ to $N_{(2)}$, i.e. the transformation (VIII) → (IX) → (X), is possible. Together with the categorical view that azoxy-arenes are incapable of such transformation[85–87], reports claiming to demonstrate the possibility of the migration of oxygen in individual instances are being constantly published[92–94,99,100]; for a discussion of this question, see Refs.71, 72, 87, and 99.

The attempt to isolate aliphatic-aromatic oxadiaziridines (IX, R = Ph, R^1 = Me, or Et) in the photoisomerisation of the azoxy-compounds (VIII) and (X) was also unsuccessful. However, the fact that the photolysis of compound (VIII) yields compound (X) and that the addition of O_2 does not affect the results of photolysis apparently indicates the intermediate formation of compound (IX).[101] The difficulty of isolating oxadiaziridines with aryl substituents can be understood if account is taken of the lability of the analogous *N*-aryloxaziridines in relation to the *N*-alkyl derivatives[102,103]. However, it is remarkable that the azoxy-compounds (X, R = Ph, R^1 = Me or Et) are not converted into compounds (VIII),[101] while the latter are the main products of the oxidation of the corresponding diazenes[104].

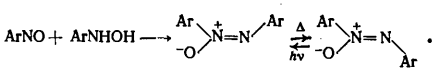
The attempts to synthesise oxadiaziridines with alkyl substituents were more successful. Compounds (IX, R = R^1 = t-Bu,[81,105] n-Bu,[81] or iso-Pr[106]) were obtained by the photolysis of the corresponding azoxy-compounds, into which they are reconverted at the usual temperatures with a half-life of several hours. The oxadiaziridine (IX, R = Me, R^1 = t-Bu) proved to be unstable[81] and *cis*-oxadiaziridine is not formed on photolysis of compound (VII).[81] In a recent study[107] the methods of synthesis and the properties of oxadiaziridines were carefully investigated.

The possibility of the migration of oxygen in the azoxy-sulphones (VIII, R = Ar, R^1 = SO_2Ar^1) via the intermediate formation of an oxadiaziridine has been examined[108,109] (cf.Neiman et al.[86]).

The second type of isomerism of azoxy-compounds, namely *cis*(*E*)–*trans*(*Z*) isomerism, is a consequence of the double bond between the nitrogen atoms. In the acyclic series *cis*-azoxy-compounds are obtained by the photochemical isomerisation of the corresponding *trans*-isomers[70,87–91,93,97–99,106,107,110] or by the oxidation of the *cis*-azo-compounds at reduced temperatures[95,97,106,111,112].

Having analysed the initially seemingly puzzling results of Reisserts's study[113], Muller and coworkers[114,115] showed that the condensation of hydroxylamines with nitroso-compounds in an alkaline medium yields a mixture of *cis*- and *trans*-azoxyarenes, while under neutral conditions only the

trans-isomer is formed:

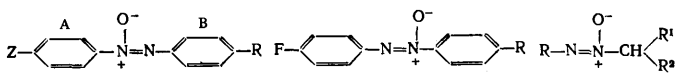


The validity of the structural assignments for pairs of isomers has been confirmed[116-118], but the influence of the pH of the medium has not so far been satisfactorily explained[119].

Aliphatic *cis*-azoxy-compounds can be obtained in a mixture with the *trans*-isomers by the thermolysis of acid-catalysed opening of the oxadiaziridine ring[106,107]. The observation that the azoxidation of *trans*(*Z*)-azoisopropane yields a certain amount of the *cis*(*E*)-azoxy-derivative together with the *trans*-isomer is also remarkable[107].

Acyclic *cis*-azoxy-compounds are unstable substances which are converted into the *trans*-isomers at the usual or slightly elevated temperatures. The mechanism of this transformation is obscure, but is apparently analogous to the *cis*–*trans* isomerisation of azo-compounds[87,98]. The instability of the *cis*-azoxy-compounds is associated solely with their easy conversion into the *trans*-isomers and not with the loss of functionality. Skeletal azoxy-compounds, in which the *cis*–*trans* transition is impossible, are highly stable[120] and can be obtained by various methods—by oxidising the N = N compound, by the interaction of vicinal nitrogen-containing groups, etc. A reliable method now exists for the identification of *cis*-azoxy-compounds, which made it possible to correct individual erroneous assignments to the *cis*-series[20,101,121]; nevertheless, acyclic *cis*-azoxy-compounds are still being inadequately investigated.

The third type of isomerism—the isomerism based on the position of the nitrogen atom at $N_{(1)}$ or $N_{(2)}$—is a consequence of the asymmetry of azoxy-group. Thus ring A in azoxybenzene (XI, Z = R = H) is deactivated in relation to electrophilic reactions; on the other hand, ring B is readily brominated, nitrated, etc.[61-64,68,69] and the azoxy-group in the distal position acts as an *ortho-para*-directing substituent, while in the proximal position it is *meta*-directing. The transmission of electronic effects via the conjugation chain in compounds (XI, Z = F) and (XII), determined from the chemical shifts of the ^{19}F signal in NMR spectra, takes place with different transmission factors and confirms the anisotropy of the polarisability of the π-system of the azoxy-group[112,122]. In aliphatic compounds (XIII) the group R in the distal position exhibits a tendency towards homolytic elimination[123], while the group RR^1CH in the proximal position can be converted into a functional group, for example, via the corresponding carbanion, and then subjected to classical addition, dehydration, etc. reactions[80]:



(XI) (XII) (XIII)

The need to synthesise substances with specific properties is dictated by the necessity to solve the problem of the location of the oxygen atom in azoxy-compounds. Infrared and ultraviolet spectroscopic methods are hardly useful for this purpose. In the aliphatic series the structural assignments of the *trans*-isomers are based on Freeman's classical study[104] using ^1H NMR; the systematic data of Snyder et al.[124] and also those of Taylor and coworkers[107,119] may prove useful for the *cis*-isomers. In the case of azoxyarenes the chemical shifts of the protons in the *o*- and *p*-positions as well as the signals of the methyl groups in the *p*-positions (for example, in azoxytoluene) are different as a result of the distal and proximal orientations of the aryl substituents[53,95,125]. ^1H NMR using shift reagents is more fruitful[53,54,126-128]. Few mass-spectrometric data are available as yet[125,129-134].

It is now possible to distinguish certain approaches to the solution of the problem: firstly, the search for new specific methods of synthesis which do not require structural proof for each individual compound; secondly, the determination of the general characteristics of the synthetic reactions in order to unify the methods for the separation and identification of the isomers. By combining all these tasks, investigators are developing methods for the simplest and fastest determination of the structure, which is demonstrated by the spectroscopic studies quoted above.

IV. OXIDATION OF AZO- AND HYDRAZO-COMPOUNDS

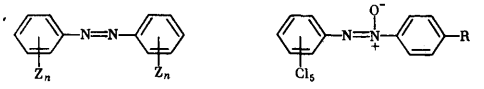
The oxidation of azo-compounds by peracids is preparatively the most convenient method for the introduction of the azoxy-group. Starting with the studies of Angeli[135-139], this procedure has been frequently used by a number of workers (see the relevant reviews of the early studies[68,69,140]). The reaction is equally applicable to aromatic and aliphatic compounds and the oxidation of *cis*- and *trans*-azo-compounds proceeds with retention of the geometry of the N = N bond[63,95,106]. The oxidation of azoarenes has been most fully studied; the investigations by Badger and coworkers[111,141,142] played a major role in explaining the mechanism of this process. It was shown that the oxidation of azobenzenes[111,141] and other azoarenes[142] by perbenzoic acid is a bimolecular reaction, the rate of which increases with electron density at the nitrogen atoms. The introduction of electron-donating substituents increases and that of electron-accepting substituents decreases the rate of oxidation, the rate constant being satisfactorily correlated with the Hammett σ constants[141] (apart from some deviation of the points for *p*-NO_2 and *p*-MeO, the best correlation was achieved with the σ* constants[143]). The oxidation of *cis*-azobenzene is 50–60 times faster than that of the *trans*-isomer and the ratio $\lg(k_{cis}/k_{trans})$ is fairly constant in the range 20–30 °C. Badger and coworkers explained this by the fact that the *trans*-azobenzene molecule is planar and there is a possibility of the delocalisation of electrons over the entire conjugation chain. Owing to the steric interaction of the phenyl groups, in the *cis*-isomer they are displaced from the plane of the azo-group by 56° and the coplanarity of the system is infringed[111] (see also, Webb and Jaffe[95] and Mitchell and Phillips[112]). This decreases the degree of conjugation and the localisation of electron density at the neighbouring nitrogen atoms, which leads as a consequence to an increase of the rate of interaction with the electrophile (the peracid)†. [111]

The influence of two substituents in the *m*- and *p*-positions in azobenzene on the rate of oxidation corresponds to the expectation based on the sum of their σ constants. The oxidation of 2-(2-naphthyl)-1-phenyldiazene yields a mixture of

† The difference between the heats of formation of the *cis*- and *trans*-isomers of azobenzene is approximately 10 kcal,[144] makes an additional contribution to the free energy of activation, and explains the increase of the rate of oxidation of the *cis*-isomer. The corresponding quantity for stilbene is small (3.0 kcal),[145] which is reflected in an insignificant difference between the rates of epoxidation of its *cis*- and *trans*-isomers[146,147].

isomeric azoxyarenes in proportions corresponding to the ratio of the rate constants for the oxidation of the individual azobenzene and 2,2′-azonaphthalene[142].

The conclusion that the oxidation of the N=N bond by peracids has an electrophilic mechanism was supported by experimental findings in a number of subsequent studies. Thus azobenzenes# (XIV) were not oxidised by the peracids usually employed (performic, peracetic, and perbenzoic) and only trifluoroperacetic acid converted them into azoxybenzenes. Similarly, compound (XV) [125] is obtained on treatment with this oxidant, while other oxidants give rise to its formation at a low rate and only at elevated temperatures.

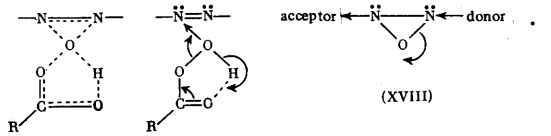


(XIV) (XV)

$Z_n = F_5$[148] (cf.[149]); $Z_n = F_4$[148,149]; $Z_n = Cl_5$[125] (cf.[150]).

Since the oxidising capacity of the peracid varies in parallel with the pK_a of the corresponding acid (the acyloxy-anion of a strong acid is more stable and is therefore satisfactorily eliminated), it follows that, among all the peracids, CF_3COOOH is the strongest oxidant[151]. The need for its employment arises as a consequence of the depletion of the N=N bond in electrons.

All these findings lead logically to the question whether or not the oxidation of azo-compounds involves a spirocyclic transition state (XVI) analogous to that proposed by Bartlett for the oxidation of the C=C bond[151-154] or whether the reaction proceeds via direct transfer of electrophilic oxygen to the nitrogen atom in (XVII) [96,154,155]:



(XVI) (XVII) (XVIII)

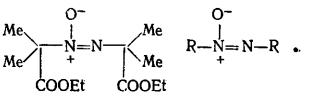
The conclusion that the addition to the N=N bond is asymmetric apparently also follows from a study[142] in which it was shown that the oxidation of azo-compounds with different substituents leads to a mixture of two isomers in proportions corresponding to their electron-donating influences. If the transition state has the symmetrical structure (XVI), then its conversion into the final product via (XVIII) leads to a ratio of isomers inversely proportional to their electron-donating influences. This idea was developed in another investigation[96].

The hypothesis of a symmetrical structure of the transition state (XVI) and the consequent possibility of the formation of oxadiaziridines was also disproved by an investigation of the oxidation of *cis*-azoarenes[95]. Among aliphatic compounds, where the stability of oxadiaziridines is sufficiently high for their identification[81,101,107], the low-temperature oxidation of azo-t-butane, for example, yields the azoxy-compound immediately, which was demonstrated by infrared spectroscopy[81] (see also Taylor et al.[107]).

At the present moment the question of the structure of the transition state in the oxidation of the N=N bond by peracids must be regarded as resolved in favour of the asymmetric structure. Comparison of the rate constants for the oxidation of stilbenes[146,147,151] and azobenzenes[111,141] showed that the latter are oxidised at a rate higher by an order of magnitude. This may also constitute a piece of evidence showing that the interaction of the electrophilic oxygen with a free electron pair is preferred to the interaction with the π-electron system. The electrophilic oxidation of different heteroatoms (N, P, and S) has been considered in a number of studies[154,155] and analysis of the available data shows that it is usually faster than epoxidation. In full conformity with this observation, it was found[156,157] that the oxidation of compounds with the C=C–N=N or C=C–C–N=N structural unit leads to azoxidation and not to the formation of epoxides.

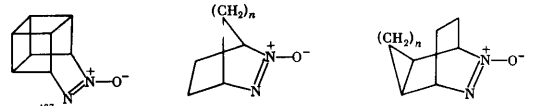
The oxidation of the N=N bond by peracids is widely used in practice, particularly for the synthesis of azoxyarenes (see the relevant reviews[61-64,68,69,74-76,140], the examples already quoted, as well as a number of other communications[158-178]).

Azoxidation has been used much less among aliphatic compounds. Thus Aston and Parker[179] were the first to obtain a ditertiary azoxy-compound (XIX) by treating an azo-compound with the H_2O_2 + MeCOOH mixture:



(XIX) (XX)

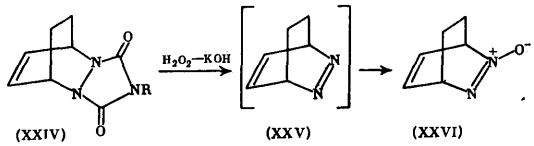
Subsequently, it was shown that this oxidising mixture is sometimes unsuitable for the preparation of diprimary and disecondary azoxy-compounds, since the transformation of the initial azoalkanes into hydrazones, catalysed by acetic acid, is faster than azoxidation. The difficulty was overcome by employing aromatic peracids, for example, perbenzoic acid; a satisfactory yield of the corresponding azoxy-compounds (XX, R=Me, n-Pr, iso-Pr, or $PhCH_2$) was then obtained[3,4]. The fact that the MeCOOH + H_2O_2 mixture is not equivalent to MeCOOOH has been frequently mentioned[151]. The employment of the former creates an excess acidity of the medium owing to the high concentration of MeCOOH at the beginning of the reaction and the slow stage involving equilibration with the peracid. It is therefore not surprising that azoisobutane (XX, R=iso-Bu) (disecondary azoalkane) was oxidised smoothly under the influence of MeCOOOH.[104] Evidently, both peracetic and perbenzoice acids are very suitable for the oxidation of ditertiary and disecondary azoalkanes. The oxidation of diprimary azoalkanes, for example, azobutane and particularly compounds of the type of ω-azotoluene, where the possibility of a prototropic transformation into hydrazones is facilitated, requires the use of aromatic peracids[104,180]. The use of trifluoroperacetic acid may be complicated by secondary reactions of the latter with azoxyalkanes[81,181,182]. Compounds are known in which the structural unit N=N(O) is a partly aromatic system (see, for example, a number of reviews[183-185]). In 1962 Freeman also obtained several Δ^2-pyrazoline *N*-oxides[186], which are isomeric with azoxy-compounds. Nevertheless, the ease with which cyclic azo-compounds are oxidised to skeletal azoxyalkanes (XXI–XXIII) and the high thermal stability of the latter were found to be somewhat surprising.



(XXI)[187] (XXII), $n = 1$[84]; $n = 1$-4[124,188,189] (XXIII), $n = 1, 2$[124,188,189]

Here and throughout the review the *trans*-configuration of the azo- and azoxy-compound is understood unless stipulated otherwise.

In order to obtain the azoxyalkanes (XXI)–(XXIII) as well as certain others, for example (XXVI), bicyclic and polycyclic triazolinediones were oxidised with hydrogen peroxide in an alkaline medium[120,188–190]:

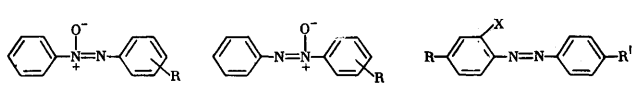


A similar synthetic procedure, involving the removal of the protective group with simultaneous oxidation, had been used earlier to synthesise 3-alkyldiazirines[191,192], since the latter are not oxidised further to the corresponding azoxy-compounds[193] (see also, Snyder et al.[120]). However, the azo-compound (XXV), which could have been a precursor of compound (XXVI), is extremely unstable (the decomposition period at −78 °C is ≤30 s), while the transformation (XXIV) → (XXVI) proceeds at much higher temperatures (80–100 °C). Evidently, azoxidation in an alkaline medium involves a sequence other than (XXIV) → (XXV) → (XXVI).[120,124]

Apart from triazolinediones, other precursors of azo-compounds, for example dialkyl- or diaryl-hydrazines, can be oxidised. *sym*-Disubstituted hydrazines are oxidised even on storage in air; various oxidants, including H_2O_2, are used to convert them into azo-compounds[194–196]. It is therefore natural that azoxyarenes are obtained by the single-stage oxidation of hydrazobenzenes with an excess of a peracid[197,198]. It is of interest that, for a 1:1 reactant ratio, an azoxy-derivative may be formed together with the azo-compound[198], apparently because the rates of oxidation of the NH–NH and N=N groups are comparable.

A serious obstacle to a more vigorous synthetic employment of the oxidation of azo-compounds or their precursors is the formation of isomers with different positions of the *N*-oxide oxygen. As early as 1911, Angeli concluded that the oxidation of 3- and 4-nitro-azobenzenes does not yield individual substances[136,137]; this conclusion was later confirmed[99,171–173,197].

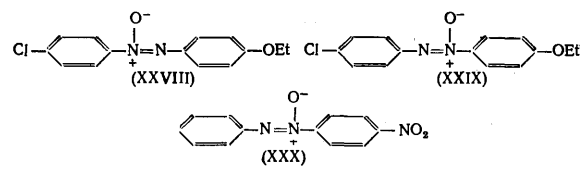
Two reviews[68,69], giving a systematic account of early data, and numerous reports by Italian chemists[136–139,158–173] quote tens of examples of the formation of a mixture of azoxyarenes in the oxidation of azobenzenes by peracids, but the lack of a quantitative estimation of the isomeric composition greatly reduces the value of these studies. Kinetic measurements of the rates of oxidation of azo-compounds seemingly suggested the possibility of estimating the ratios of the isomers from the σ constants of the substituents in azobenzenes[141,142] (see also, Mitsuhashi[96]). However, Risaliti[172,173] found that, although electron-accepting groups do direct the oxidation preferentially to the distal position, there is no linear relation between the ratios of the isomers and the σ constants:



R = *m*- and *p*-NO_2, SO_2Ar, NHAc, F, Cl, or Br.

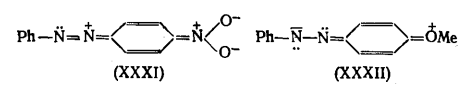
The picture is more complex for disubstituted azobenzenes. Thus it has been shown[54,199,200] that, when compounds (XXVII, X = H) with substituents R and R^1 = H, Me, MeO, COOR, or Cl in different combinations, are oxidised, the standard ratio of the isomeric azoxy-benzenes (1:1) is hardly altered. The explanation of these data requires the use of more detailed features of the azo-group and leads to a fairly complex picture. Firstly, the authors of the above reports[54,199,200] worked with the H_2O_2–MeCOOH–(H_2SO_4) § mixture, while the kinetic experiments were performed with perbenzoic acid[96,141,142] and Badger[111] emphasised specially that perbenzoic acid did not contain even an admixture of benzoic acid. Evidently, in the presence of acids stronger than acyl hydroperoxides, the nitrogen atom of the asymmetrically substituted azoarenes, which should have been preferentially azoxidised, is protonated (and hence blocked). The sum of these effects leads to an average ratio of the isomers. This hypothesis is supported by the finding that, in the presence of the chelate dipivaloylmethanemolybdenum(VI), t-butyl hydroperoxide oxidises 4-methoxyazobenzene exclusively to a single isomer[133]; the mechanism of the action of this oxidant is analogous to the mechanism of electrophilic oxidation by peracids, but the reaction is not complicated by protonation. At the same time peracetic and perbenzoic acids lead to a mixture of azoxy-compounds.

Other observations which can be interpreted from these standpoints have also been made. Thus the oxidation of 4-chloro-4′-methoxyazobenzene with hydrogen peroxide in 100% acetic acid yields compound (XXVIII), while the isomer (XXIX) is formed in 80% acetic acid[201]:

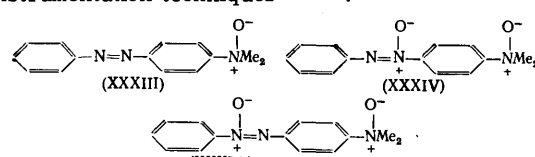


The oxidation of 4-nitroazobenzene with 30% H_2O_2 in acetic acid similarly gives a mixture in which the α-isomer (in Angeli's terminology) of compound (XXX) predominates, while anhydrous hydrogen peroxide in acetic acid gives preferentially the β-isomer[99].

Secondly, the presence of groups similar to NO_2 and MeO in the *p*-position leads to an appreciable contribution of the boundary structures (XXXI) and (XXXII) to the ground state of substituted azobenzene. Evidently, the nitro-group deactivates both nitrogen atoms, but the distal atom is deactivated much less; the methoxy-group activates both positions, but the distal position is activated to a much greater extent. Accordingly, in the azoxidation of *p*-nitro- and *p*-methoxy-derivatives (XXXI) and (XXXII) the distal isomer predominates in both cases[133]:



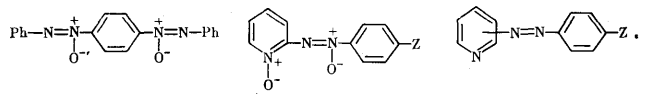
The difficulty of taking into account all these factors is effectively illustrated by the oxidation of *p*-dimethylamino-azobenzene. Starting with the work of Angeli in 1915, who attributed structures (XXXIII) and (XXXIV) to the monoxidation and dioxidation products[68,202], there have been periodic attempts to explain the course of these reactions in terms of the new advances in the electronic theory of structure and instrumentation techniques[203–207]:



§ The mixture H_2O_2–MeCOOH to which small amounts of sulphuric acid have been added is sometimes used in the synthesis of azoxyarenes without isolating peracetic acid by distillation.

Whereas the structure of the primary oxidation products (XXXIII) gives rise to no doubts so far, the views of investigators diverged as regards the dioxidation product, which can have structure (XXXIV) [68,202,205,207] or (XXXV) [204,206].

The divergence of views concerning the directing effect of the dimethylamine oxide group extends also to other instances. The azoxy-group is an electronic analogue of the $Me_2\overset{+}{N}\overline{O}$ group and, since Angeli attributed structure (XXXIV) to the product of the dioxidation of dimethylaminoazobenzene, he defended formula (XXXVI) also for the product of the dioxidation of bisazobenzene[208,209]:

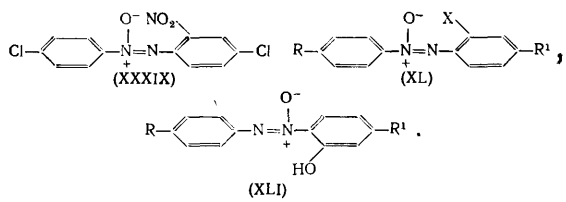


(XXXVI) (XXXVII) (XXXVIII)

According to other investigators, the dimethylamine oxide group directs oxidation to the distal position. Therefore its analogues, for example, the pyridine oxide group, act similarly and azoarenes (XXXVIII, Z = H [210-214] or NO_2 [215]), in which the nitrogen atom in the pyridine ring is oxidised first, give rise to the azoxy-derivatives (XXXVII).

The competitive involvement of nitrogen atoms in the oxidation of the compound (XXXVIII, Z = NMe_2) by peracids is of interest. The nitrogen of the NMe_2 is oxidised first, being followed by the nitrogen of the pyridine ring, while the N = N bond is unaffected[216]. Certain examples of competitive oxidation processes have been examined in a review[69].

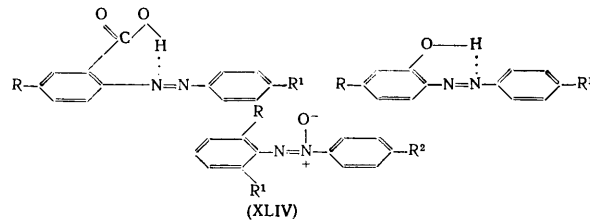
An important feature of the oxidation reactions of azoarenes is the marked influence of *ortho*-substitution on the position of the *N*-oxide oxygen atom. The influence of *ortho*-substitution (OH, COOMe, OCOPh) on the course of the oxidation of azoarenes was first investigated by Bigiavi and coworkers[159-163], but they did not obtain an unambiguous result. Other investigations were more decisive in this respect[54,197,217,218]. It was shown, for example, that the azoxybenzenes (XXXIX), (XL), and (XLI) are formed as the sole products in the oxidation of the corresponding azobenzenes:



(XXXIX) (XL)

(XLI)

These seemingly relatively incompatible results were explained and developed by Berwick and Rondeau[54]. They found that, in the presence of the *ortho*-substituents X = Me, MeO, Cl, COOMe, or COOH in one of the aryl groups, azobenzenes give rise preferentially to isomer (XL) with the distal location of the oxygen atom relative to this group regardless of the nature of R and R^1. The selectivity (the quantity defined as the ratio of the isomers formed with the distal and proximal location of the oxygen atom) varies for different X and, although the effective volume of the COOMe group is greater than that of COOH, the process selectivity is greater in the presence of COOH than in the case of COOMe. The influence of the *o*-hydroxy-group, which caused a complete rearrangement of the position of the oxygen atom in favour of the proximal isomer (XLI) is still more surprising. All these findings were explained by Berwick and Rondeau[54] (see also Dziomko and Dunaevskaya[217]) by the fact that the influence of the *ortho*-substituent is in general related to the shielding of the neighbouring nitrogen atom. On the other hand, the introduction of specific substituents (COOH, HO), capable of forming a hydrogen bond with the N = N group, increases the selectivity of the β-oxidation (for COOH) or, on the contrary, leads to a complete rearrangement (for the OH group) ¶:

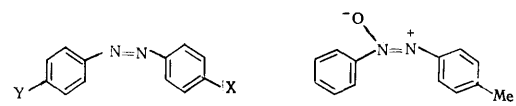


(XLIV)

Protonation of the distal nitrogen atom (and hence its deactivation in relation to oxidation) creates an unprecedented situation where the group in the *ortho*-position directs oxidation to the proximal position[54,217]. It is therefore natural that the oxidation of 2-alkyl-2'-hydroxyazoarenes yields exclusively a single isomer[217].

In the presence of two substituents in the 2- and 6-positions in the phenyl group, their directing effect is greatly enhanced and the oxidation of such azo-compounds by peracids[167,222] or the CrO_3–HNO_3 mixture[223,224] leads to only the distal isomer (XLIV).

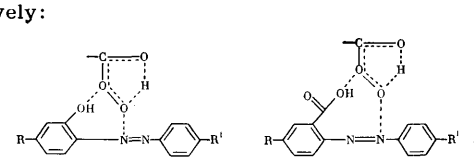
In the oxidation of the *cis*-azoarene (XLV, Y = H, X = Me) it was possible to isolate only one isomer (XLVI). However, it was shown that both isomers are formed in reality, but the azoxy-compound with the proximal location of oxygen in relation to the tolyl groups is converted much more readily into the corresponding *trans*-isomer and compound (XLVI) and it was therefore not possible to identify it[95]:



(XLV) (XLVI)

In the oxidation of compounds (XLV, Y = F, X = Me, MeO, or CF_3) one isomer was also obtained; it was postulated that the oxygen atom is located in the proximal position relative to the fluorine-containing aryl group[112]. In the case of *cis*-azoarenes (XLV, Y = H, X = Cl or Br) only one *cis*-azoxy-compound was also isolated, but its structure was not determined[95].

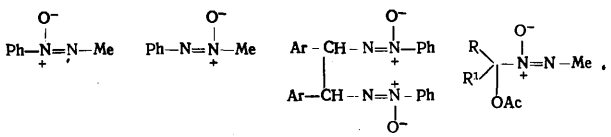
¶ Another explanation of the directing effect of hydroxyl-containing substituents can be the acceleration of the azoxidation of the N = N bond in the proximal (for the OH group) or distal (for COOH) position as a result of the additional stabilisation of the transition complex (XLII) or (XLIII) respectively:



(XLII) (XLIII)

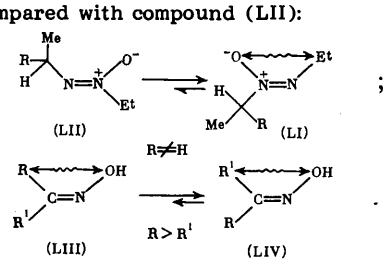
The formation of a hydrogen bond facilitates the elimination of the anion. Examples of the acceleration of the reactions by neighbouring groups as well as the consequence of hydrogen bonding in the epoxidation of allyl alcohol, *o*-allyl-phenols, etc. are well known[219-221].

The problem of the location of oxygen in the oxidation of aliphatic-aromatic azo-compounds and asymmetric azoalkanes by peracids has not been studied systematically and only a few observations have been made. The oxidation of methylphenyldiazene yields predominantly the azoxy-compound (XLVII) with a small admixture of the isomer (XLVIII)†.[104] Similarly the azoxy-compound (XLIX) was obtained in the oxidation of the bisazo-compound[121] and the location of oxygen agrees with Freeman's data[104], already quoted, concerning the preferential formation of compound (XLVII) compared with compound (XLVIII):



(XLVII) (XLVIII) (XLIX) (L)

The oxidation of α-acetoxyazoalkanes gives rise to azoxy-compounds [L, $R = R^1 = Me$, $R, R^1 = (CH_2)_5$],[226] although the oxygen atom in the natural products macrozamin[2-5] and cycasin[9,12,13,21], containing methylazoxymethanol as the aglycone, is located in the proximal position relative to the methyl group and not in the distal position as in compounds (XLVII) and (L). In this connection one should recall that irradiation at 254 nm of the azoxyalkanes (LI) or (LII) in hexane leads to a steady-state mixture of two isomers in the proportions (LI) : (LII) = 1.28,[227] which reflects the weak steric interactions of the alkyl group with the oxygen atom in compound (LI) compared with compound (LII):

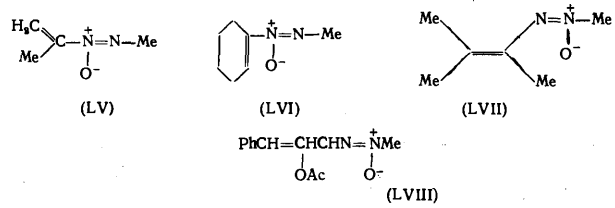


(LII) (LI) (LIII) (LIV)

Similarly the Z-configuration (LIV) is preferred in the case of the ketoximes (LIII) and (LIV).[228]

The question of the stability of the isomeric azoxyalkanes for asymmetric substitution at the $N_{(1)}$ and $N_{(2)}$ atoms, arising in the photochemical reactions and on opening of the oxadiaziridine ring, has been discussed[107].

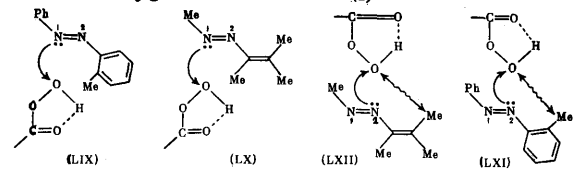
The natural antibiotics and carcinogens elaiomycin[5,6] and LL-BH872α [18-20] are α,β-unsaturated azoxy-compounds and this is why several studies have been devoted to the oxidation of model compounds with the structural elements N=N–C=C and N=N–C–C=C. The corresponding azoxy-compounds (LV)–(LVII) [156] and (LVIII) [157] were obtained, but the regioselectivity of the oxidation process was not discussed by the authors:



(LV) (LVI) (LVII)

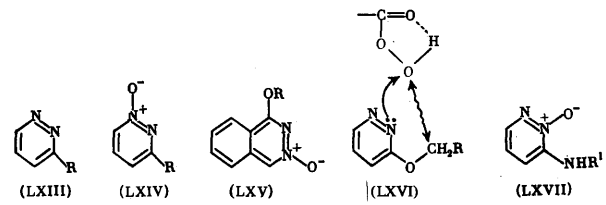
(LVIII)

All these data on the oxidation of aliphatic and aliphatic-aromatic azo-compounds do not throw light on the question which factors determine the attack by oxygen of a particular nitrogen atom in the N=N bond, namely the inductive, resonance, or steric effects of the substituents. Nevertheless, many experimental data concerning the isomeric composition of azoxy-compounds can apparently be explained on the hypothesis that the location of oxygen in azoxidation is determined by the kinetic parameters of the irreversible reaction and is strongly subject to the steric effect of the groups located at the N=N bond. Distal groups have a weak influence in the approach of electrophilic oxygen [see compounds (LIX) and (LX)], while the influence of the proximal group is more significant [see compounds (LXI) and (LXII)] and in the oxidation reactions of the azo-compounds listed below oxygen is located at $N_{(1)}$:



(LIX) (LX) (LXII) (LXI)

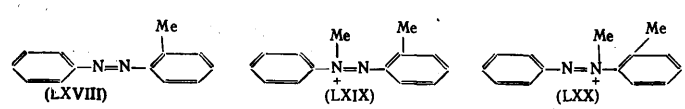
Data for the oxidation of 3-substituted pyridazines (LXIII) [185,229] confirm the marked influence of the substituent on the course of oxidation. For example, when R = Me, a mixture of *N*-1- and *N*-2-oxides is obtained[185,229,230], while for R = MeO, EtO, PrO, or $C_6H_5CH_2O$,[185,229-233], the products are only the *N*-1-oxide (LXIV). The oxidation of 1-alkoxyphthalazines yields the *N*-3-oxides (LXV) [229,234,235].



(LXIII) (LXIV) (LXV) (LXVI) (LXVII)

The structure (LXVI) is not formed [cf. (LXI) and (LXII) [54,197,217]]. The 2-oxide (LXVII) is formed exclusively from the compounds (LXIII, R = NH_2 [185,229,236-239] or NHR [1,185,229,240]), and the analogy with the proximal directing effect of the *o*-hydroxy-group in the oxidation of azoarenes[54,217] is evident.

It is of interest to compare the azoxidation reaction with other processes involving electrophilic addition to the N=N bond. Thus Fergusson[241] investigated the quaternisation of azoarenes by methyl fluorosulphonate and found that the azoarene (LXVIII) gives rise to a mixture of isomers (LXIX) and (LXX). The distal isomer is known to predominate appreciably in azoxidation[54].



(LXVIII) (LXIX) (LXX)

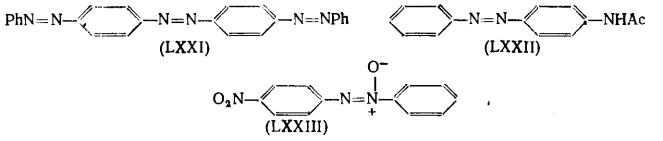
This can be explained by the fact that the quaternisation is a reversible reaction and leads to a product ratio determined by process thermodynamics, while azoxidation is irreversible and the final isomer ratio reflects the results of a kinetically controlled reaction. A comparative study of the steric factors in the oxidation and quaternisation of pyridines has been described by Foucart et al.[242].

The irreversible nature of the azoxidation reaction has been confirmed experimentally. For example, the oxidation of methylphenyldiazene yields the isomer (XLVII),[104] which is converted by photolysis into the isomer (XLVIII).[101] Since

† We may note incidentially that the oxidation of phenylazoformamide yields $PhN(O)=NCONH_2$,[48,225], i.e. oxygen is also located at the nitrogen atom of the aryl group.

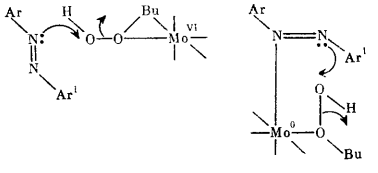
equilibrium conditions are apparently obtained on irradiation of azoxy-compounds and substance (XLVIII) cannot be converted into (XLVII),[101] the isomer (XLVIII) is evidently thermodynamically more stable than the isomer (XLVII).

Apart from the difficulty of identifying the structural isomers, the peracid method suffers from yet another disadvantage, associated with the effect of the peracid on other functional groups. Thus the oxidation of 4-aminoazobenzene involves primarily the amino-group and the product is trisazobenzene (LXXI).[243] The latter can be oxidised further, giving rise to monoazoxybisazobenzene and trisazoxybenzene[243,244]:



Protection of the amino-group by the acyl group in compound (LXXII) favours the "normal" oxidation of the N = N bond with formation of the proximal and distal isomers[243], but in this case nitroazoxyarene (LXXIII) is formed as a side product owing to the hydrolysis of the amide linkage[169,170,245]. Several examples of secondary reactions in azoxidation were examined above and are dealt with more fully in Bigelow's review[69].

Apart from peracids, other reagents have also been used occasionally for the azoxidation of the N = N bond. A remarkable variant of the peracid method is oxidation of azo-compounds by alkyl hydroperoxides in the presence of transition metal complexes[133]. Coordination to transition metal complexes causes the polarisation of the O—O bond and the peroxides, which are usually homolysed at this bond, become sources of electrophilic oxygen[153,246-249]. The complexes $Mo^{VI}[MoO_2(dipivaloylmethane)_2]$ or $Mo^0[Mo(CO)_6]$ with t-butyl hydroperoxide oxidise substituted azobenzene to azoxy-compounds, while vanadium(IV), manganese(III), and cobalt(II) complexes, which promote the homolytic decomposition of t-BuOOH, proved to be inert[133] (for the principles of the selection of the transition metal, see Gould et al.[249]). Two different types of transition states, taking into account the selectivity in the location of oxygen at the N = N bond for the molybdenum(VI) complex and the statistical distribution of the isomers for zero-valent molybdenum, have been proposed:

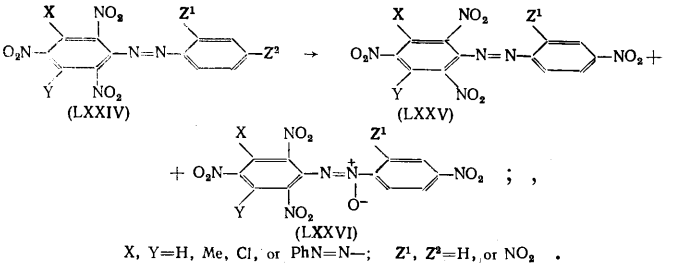


The involvement of transition metals and mild reaction conditions constitute a similarity between these processes and those in living organisms, and, together with the oxidation of diacylhydrazines to azoxyalkanes, by-passing the azo-compound stage[120,124], and the fixation of oxygen by hydrazyl radicals[250], demonstrates the multiplicity of pathways leading to the formation of the N = N(O) group under conditions close to those in biological systems. A number of azoxy-compounds[2-21] and those formed in the microbiological or photochemical oxidation of amines[251-253] can be obtained not only by the classical reaction between RNO and RNHOH, but also by the direct microsomatic oxidation of azo- and hydrazo-groups by *N*-oxidase. The detection of the familiar carcinogens and mutagens azoxymethane and methylazoxymethanol in the product of the metabolism of 1,2-dimethylhydrazine evidently demonstrates the validity of this point of view[254,255]. The general problems of the biogenetic relations in the series of nitrogen-containing functional groups have been examined in a number of studies[17,22].

The azoxidation of the N = N bond in the nitration of azobenzenes was first reported by Petriew[256] and this observation was confirmed by subsequent studies[223,224,257-261]. The nitration process is normally accompanied by the formation of the *p*-isomer, but if both *p*-positions are blocked, as in 4,4'-dichloro-[257,260] or 4,4'-dinitro-azobenzene[259], then, together with nitration products, the *o*-azoxy-derivative is formed.

The formation of 2,4,3'-trinitroazoxybenzene in the nitration of azobenzene[258] has also been reported (cf. Sharnin and Buzykin[223]; for the review of early studies on the nitration of azo- and azoxy-arenes, see, Werner and Stiasny[259]). Among aliphatic compounds, oxidation by nitric acid has been used to synthesise azoxycyclohexane from azocyclohexane[3], but a negative result was obtained for 1-azoheptane and 2-azopropane[4]. When the menthylhydrazone of menthone was treated with nitric acid, the product was azoxymethane[262].

A detailed study showed[223,224] that the nitration of azoarenes (LXXIV) by various reagents (98% HNO_3, HNO_3–H_2SO_4, and HNO_3–CrO_3) leads to mono- and dinitration products (LXXV) and also to azoxy-derivatives (LXXVI):



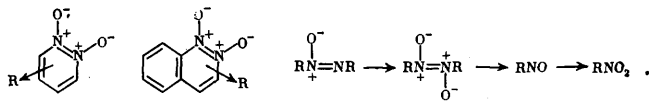
X, Y=H, Me, Cl, or PhN=N–; Z^1, Z^2=H, or NO_2 .

Sharnin and Buzykin[223,224] observed several interesting features: (1) the azoxy-compounds (LXXVI), with a distal location of oxygen relative to the picryl group, are formed in oxidation processes; (2) the azo-compounds (LXXIV, $Z^1 = NO_2$, Z^2 = H or NO_2) do not give rise to azoxy-compounds at all or produce them with much difficulty under the influence of the most powerful oxidant ($CrO_3 + HNO_3$); (3) the accumulation of electronegative substituents in the picryl ring of compounds (LXXIV, X, Y = Cl) hinders the formation of azoxy-compounds.

Evidently, these features are the same as those in the electrophilic oxidation of azoarenes by peracids, in particular the pronounced directing effect of the *ortho*-substituent, the retardation of oxidation in the presence of 2,2'-substituents, the distal directing effect of electron-accepting groups at the N = N bond, and the need for a more "electrophilic" oxidant on accumulation of electronegative substituents at the N = N bond. All this apparently constitutes evidence supporting an electrophilic mechanism of oxygen transfer to the azo-group.

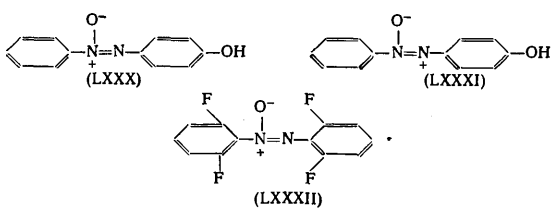
The formation of azoxy-compounds is observed in the oxidation of azo- and hydrazo-arenes by chromium trioxide in MeCOOH,[256] dimethyl sulphoxide at 110 °C,[198] ozone,[263] hydrogen peroxide[188-190,264,265] (cf. Singh[182]), and a mixture of hydrogen peroxide and sodium tungstate[266]. Studies have been published on the use of polymers containing peracid groups for the oxidation of azobenzene[267,268]. Such polymers are obtained, for example, by modifying cross-linked structures with polyacrylic acid.

The oxidation of azo-compounds results in the incorporation of one oxygen atom. It is of interest to attempt to introduce also a second atom and thus form azo-dioxy-derivatives. Among heteroaromatic compounds, such cases have been described. For example, when pyridazines[269], cinnolines[270-274], and benzocinnolines[274] are acted upon by peracids under conditions more severe than those in the usual azoxidation, the dioxides (LXXVII) and (LXXVIII) are obtained together with azoxy-derivatives. The stepwise course of the process was demonstrated by the conversion of the monoxides into the dioxides under the reaction conditions[269-274]:



(LXXVII) (LXXVIII) (LXXIX)

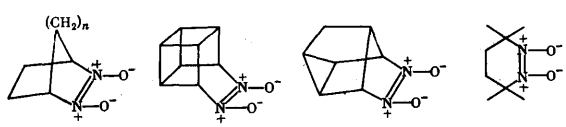
In the case of linear azoxy-compounds it is difficult to detect the individual stages, since on monomerisation and subsequent oxidation of the diazene dioxides (LXXIX) formed, nitro-compounds are produced[202]. Thus compound (LXXX) is oxidised by hydrogen peroxide to nitrophenol[158], which does not, however, demonstrate the validity of the mechanism described and can be explained by the primary effect of the oxidant on the hydroxy-group and subsequent decomposition of the quinonoid intermediate at the nitrogen–nitrogen bond:



(LXXX) (LXXXI) (LXXXII)

In conformity with this hypothesis, it has been found that, in contrast to compound (LXXX), azoxyphenol (LXXXI) is not oxidised by H_2O_2, $KMnO_4$, or HNO_2, since the azoxy-group deactivates the neighbouring aryl group[158,275,276]. On the other hand, indirect data show that the sequence azoxy-compound → azodioxy-compound → nitroso-compound → nitro-compound is possible. Thus the azoxyarenes (LXXXII) [277] and (LXXVI) (see above) are exceptionally resistant to the action of the most vigorous oxidants (CF_3COOOH, HNO_3–CrO_3), since the non-quaternised nitrogen atom is blocked by the *ortho*-substituents and its basicity is reduced due to the electron-accepting effect.

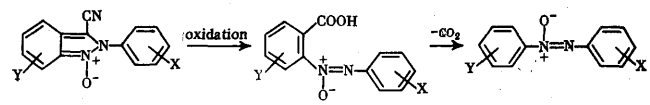
It has been shown in a recent series of studies that diazene dioxides can be obtained by the direct oxidation of the corresponding azoxy- or azo-compounds by hydrogen peroxide, *m*-chloroperbenzoic acid[189,266], and trifluoroperacetic acid[182].



An attempt has been made to explain why the usual monomerisation of nitroso-dimers does not occur in the case of highly strained rings[189,266].

V. OXIDATION OF INDAZOLES

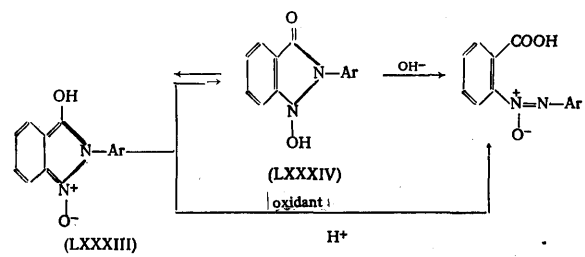
An elegant method of synthesis of azoxyarenes was developed by Behr[278,279]:



Y = H, X = 4-Br, 4-EtO, or 3-NO_2; X = H, Y = 4-Br, 4-EtO, or 3-NO_2.

The comparatively readily available 2-aryl-3-cyanoindazole 1-*N*-oxides, obtained from the corresponding *ortho*-substituted nitrobenzaldehydes (or nitriles of *o*-nitro-mandeleic acids) and arylamines (see the reviews of methods of their synthesis[280,281]) are subjected to oxidative cleavage. Starting with well known compounds, in which the positions of substituents have been determined and none of the subsequent stages of the synthesis entail the loss of asymmetry by the N=N(O) fragment, it is possible to obtain specific isomers of substituted azoxybenzenes. Behr's method played an important role in its time in the solution of this confused problem. We may note that the structural assignments of pairs of isomers of *p*-bromo- and *p*-ethoxy-substituted azoxybenzenes made by this method agree with those of Angeli.

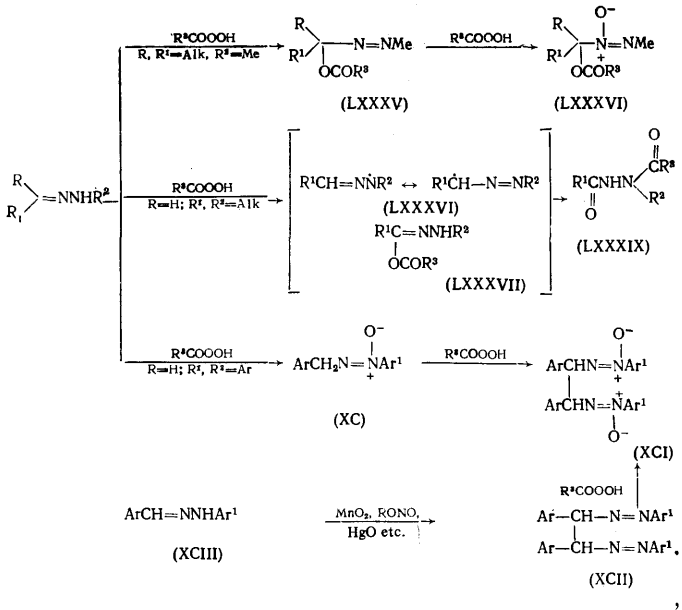
In analysing Behr's procedure for the synthesis of azoxybenzenes, one may conclude that the protection of the 3-position in indazole by the cyano-group is unnecessary since this group undergoes oxidative decarboxylation with formation of 1-hydroxyindazol-3-one (LXXXIV), which is tautomeric with 3-hydroxyindazole 1-*N*-oxide (LXXXIII). Subsequent cleavage of the tautomeric pair in an acid medium [via compound (LXXXIII)] involves the decomposition of the hemiaminal linkage and the nitrone–azoxy-migration of the double bond[186]. The oxidative hydrolysis of the N–CO bond in the intermediate (LXXXIV) proceeds also in an alkaline medium, like the oxidation of compound (XXIV):



(LXXXIII) (LXXXIV) H+

VI. OXIDATION OF HYDRAZONES

Hydrazones are isomeric with azo-compounds, but their oxidation with peracids proceeds quite differently. Typical instances are presented schematically below:



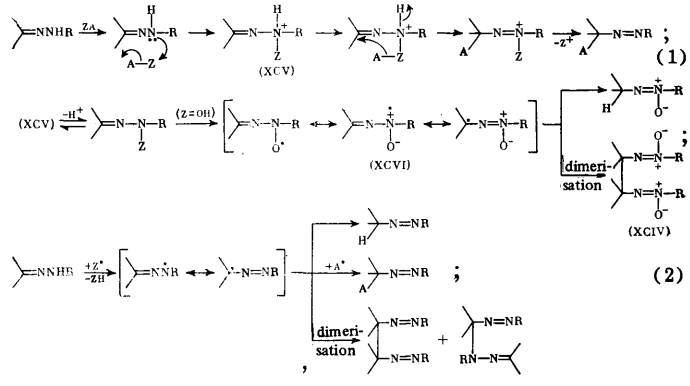
The simplest case is that of the oxidation of alkylhydrazones of ketones (acetone, cyclohexanone).[157,226]. For the ratio peracid : hydrazone = 1 : 1, a mixture of the azo-compound (LXXXV) and azoxy-compound (LXXXVI) is formed; for the reactant ratio 2 : 1, the only product is the azoxy-compound, but in a low yield (17%). The oxidation of alkylhydrazones of α,β-unsaturated ketones (cyclohexenone, cyclopentenone) with one equivalent of a peracid confirms that the primary products are acyloxyazoalkanes[157].

The oxidation of alkylhydrazones of aliphatic aldehydes does not lead to azoxy-compounds, the products being diacylhydrazines (LXXXIX).[226] Different mechanisms, involving intermediate acyloxyhydrazones (LXXXVII) or radicals (LXXXVIII), can be put forward. The oxidation of the methylhydrazone of cinnamaldehyde yields the azoxy-compound (LVIII).[157]

The oxidation of alkyl(aryl)hydrazones of aromatic aldehydes by peracids has been frequently studied[282-289]. Different structures have been attributed to the high-melting products formed as a result of the reaction and, whereas the general view inclined towards the *cis*-azoxy-compounds (XC),[154,288,289] Woodward and Wintner[121] showed that they are in reality bisazoxy-compounds (XCI). In the oxidation of the *p*-bromophenylhydrazone of *p*-chlorobenzaldehyde, they succeeded in isolating the intermediate (XC), which gave rise to a dimeric azoxy-compound (XCI) on further oxidation; thus the primary oxidation product is an azoxy- and not an azo-compound, in contrast to the aliphatic analogue[121]. Compound (XC) had been isolated earlier, but its reactions were incorrectly interpreted (see, for example, Brough et al.[288]). It is also known that the oxidation of the phenylhydrazones of aromatic aldehydes by HgO, MnO_2, $C_5H_{11}ONO$, etc. yields the bisazo-compound (XCII) (together with other products) as a result of the dimerisation of a centred radical[290-293]. The oxidation of this dimer by perbenzoic acid leads to the formation of the bisazoxy-compound (XCI), identical with the product of the oxidation of a hydrazone or the monoazoxy-compound (XC).[121]

The interaction of peracids with an NH group can be interpreted in two ways—from the standpoint of the electrophilic addition of oxygen to the nitrogen or the radical abstraction of hydrogen from the NH group. In the oxidation of the aryl hydrazones of aromatic aldehydes (XCIII) Lynch and Pausacker[286] found a direct relation between the electron-donating properties of the substituent in the aromatic ring Ar^1, linked to the extreme nitrogen atom, and a second-order reaction rate constant, which is consistent with an electrophilic oxidation mechanism (see also Pausacker[283]). However Gillis and LaMontagne[157] defended the radical mechanism involving the primary capture of the NH proton (see also Woodward and Wintner[121,292]).

Accordingly, it is possible to put forward two mechanisms# involving as the primary step the electrophilic addition of a peracid (1) or the radical capture of a hydrogen atom (2) (Z = OH, A = OCOR):



Z = OH, $Pb(OAc)_3$, OH, Hal, RC(=O)O, or NO_2;
A = OCR, OAc, OH, Hal, RCOO, or NO_2.

Mechanism (1), involving the primary (electrophilic) addition of the oxidant to the nitrogen atom, was put forward by Busch and Dietz[294] and still remains attractive. In the specific instance of oxidation by peracids this possibility is supported by the following findings: (1) in the oxidation of a secondary nitrogen atom, for example, in diarylamines, the product is a nitroxy-radical[295-298]; (2) the direct dependence of the rate of reaction of peracids on the electron density at the NH group in compound (XCIII), discovered by Lynch and Pausacker[286], is consistent with the slow stage of the bimolecular reaction (1); (3) the dimerisation of the C-centred radical, containing the complete N = N(O) functional group, leads to the bisazoxy-compound (XCIV), since the isolation of an azoxyazo-product of the monoxidation of the N = N bond in the bisazo-compound (XCII) has not been reported[121,282-289]; (4) the oxidation of the *p*-bromophenylhydrazone of *p*-chlorobenzaldehyde leads to 4,4′-dibromoazoxybenzene as a side product[121], which is apparently a dimer of the fragment obtained in the homolysis of the N = N bond in the intermediate (XCV) or (XCVI).

We may note that the oxidation of the phenyl hydrazones of 2- and 4-formylpyridines with perbenzoic acid involves the pyridine nitrogen atom[299]. The fundamental mechanisms of

Mechanisms (1) and (2) represent in a general form the mechanisms of the oxidation of hydrazones by peracids, lead tetra-acetate, hydrogen peroxide, halogens, diacyl peroxides, and nitrogen tetroxide.

the oxidation of hydrazones by various reagents have been examined in detail in a monograph[300].

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Thus the methods of synthesis of azoxy-compounds are simple and varied, which is one of the reasons for the great interest in these substances. Nevertheless, both in the series of methods considered here and among other possibilities, the oxidation of azo-compounds is used most frequently as the method of synthesis of azoxy-derivatives. The availability of the initial azo-compounds and the simplicity of the isolation of the final product make the method of practical importance. This is indicated, for example, by numerous patent data on the synthesis of azoxyarenes used as liquid crystals or forming part of such compositions.

Since this review was written, fairly numerous studies on alkoxy-compounds, mainly devoted to the practical applications of liquid crystals and to the study of their physicochemical properties, have been published. The carcinogenic properties of azoxymethane [301-308] and the influence of various substances on the inhibition of carcinogenesis[309-314] are being vigorously investigated. There is much similarity in the action of 1,2-dimethylhydrazine and azoxymethane, but the mechanism of the oxidative transformation of this pair of compounds *in vivo* is obscure; methylazoxymethanol has been detected in the products of their metabolism.

The physicochemical properties of azoxy-compounds are being vigorously investigated. The ^1H and ^{19}F NMR spectra of polyfluoroazoxybenzenes[315], the ^1H NMR spectra of partly deuterated azoxyanisoles[316], the ^{14}N and ^{15}N spectra of various compounds containing the N(O)=N fragment[317,318], and the ^{14}N NQR spectra of *p*-azoxyanisole and related compounds[319] have been studied. Calculations by the CNDO method of the spin–spin coupling constants for compounds containing single and double nitrogen–nitrogen bonds agree satisfactorily with experiment[320]. The ultraviolet spectra of azoxybenzenes[317,321] as well as the mass spectra of azoxybenzenes[321], azoxycyanides ArN(O)=NCN,[322] tetranitroazoxytoluenes[323], and compounds of the type PhN(O)=NOR, where R = alkyl or $CH_2C(OH)R^1R^2$, [324-326] have been examined.

The crystal and molecular structures of deuterated azoxyphenetole[327], *cis*-2-cyclohexyl-1-methyl- and *cis*-1-cyclohexyl-2-methyl-diazene 1-oxides[328], as well as the structure of complexes of azoxybenzenes with chloranil, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, etc.[329-331] have been studied. Calculations have been made by the CNDO method of the electron densities, dipole moments, and overall energies of various conformations of *p*-azoxyanisole[332]. The thermo- and photochemical transformations of azoxyalkanes and related oxadiaziridines have been examined[333-335]. New data have been obtained on the photochemical transformation of azoxybenzenes into 2-hydroxyazobenzenes, demonstrating the involvement of the diazonium ion in this reaction[321,336,337]. The radical decomposition of *p*-alkoxyazoxybenzenes in the solid phase under the influence of X-rays has been studied[338].

Oxidation with H_2O_2 + AcOH mixtures has been used for the synthesis of azoxyarenes having the general formula $4\text{-}RC_6H_4N(O)=NC_6H_4R^1\text{-}4$ (R and R^1 are alkyl or alkoxy-groups containing between 1 and 10 carbon atoms), which are widely used as liquid crystals, phases in GLC, dye sensitisers, etc.[321,339-344]. The addition of acid anhydrides, particularly boron trioxide, improves the process[345]. The direct oxidation of mixtures of ArNO and $ArNH_2$ to azoxyarenes, by-passing the stage involving the isolation of the corresponding azo-compounds, has been described in a patent[346]. In all these cases a mixture of isomers was usually obtained. Permaleic acid or the $H_2O_2 + CF_3COOH$ mixture is used for the synthesis of asymmetric azoxy-compounds of the type $4\text{-}RC_6H_4N(O)=NR^1$ (XCVIII), where R^1 = COOMe, CN, or C(O)Ph, which contain electron-accepting groups[347-349]. The azoxy-cyanides (XCVIII, R^1 = CN, R = alkyl, halogen, or NO_2) are of interest because of their microbiological activity[347-350].

It has been shown[351] that the one-electron reduction of $PhN(O)=NC_6H_4NO_2\text{-}4$ by potassium cyclo-octatetraenide in tetrahydrofuran does not involve the migration of the oxygen atom to the neighbouring nitrogen atom. It has also been shown that there is no exchange of ^{18}O between labelled dimethyl sulphoxide and azoxybenzene when their mixture is heated for a long time in toluene[352].

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Fluorine-containing β-Diketones

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The methods of synthesis, the keto-enol tautomerism, the chemical reactions (including the formation of heterocycles), and the applications of fluorine-containing β-diketones are examined. The influence of the introduction of fluorine-containing substituents on the properties of β-diketones is discussed.
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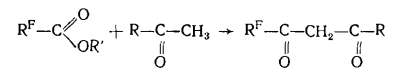
I. INTRODUCTION

β-Diketones and their metal chelates are widely used in industry and in laboratory practice as extractants and analytical reagents for the lanthanides, as shift reagents, as biologically active substances, and as catalysts of various reactions. By virtue of the presence of two carbonyl groups and their tendency towards enolisation, they lead to the possibility of investigating the keto–enol tautomerism, dual reactivity, the nature of the intramolecular hydrogen bond, and the synthesis of various heterocyclic compounds. Fluorine-containing β-diketones are in many instances superior as regards their useful properties to their non-fluorinated analogues [extraction, gas-liquid chromatography (GLC) of chelates, and biological activity] and have a number of characteristic features due to the presence of fluorine atoms in the molecule.

Extremely extensive data concerning the synthesis, chemistry, and possible applications of polyfluorinated β-diketones and heterocycles based on them have now accumulated in the literature, but the problem has not been surveyed, with the exception of a review[1] covering the literature up to 1968 and devoted to a large extent to the metal chelates of fluorine-containing β-diketones. Data on the metal chelates of fluorinated β-diketones are also contained in another review[2] and those on the applications of non-fluorinated metal β-diketonates are given in two other publications[3,4]. This review provides a survey of the literature data on the synthesis, keto–enol tautomerism, and the most characteristic synthetic reactions and practically useful properties (including biological activity) of polyfluorinated β-diketones. The literature up to 1979 inclusive is covered.

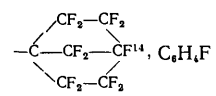
II. METHODS OF SYNTHESIS

The most common and universal method of synthesising polyfluorinated β-diketones is the Claisen condensation[5,6] using the esters of carboxylic polyfluoroacids and methyl ketones as the starting materials and sodium alkoxides[7,8], sodium amide[9,10], sodium hydride[11], and boron trifluoride[12] as the condensing agents. The condensation is usually carried out in anhydrous diethyl ether[5,6], but benzene[13], dimethoxyethane[14], dimethyl sulphoxide (DMSO),[11] and acetic acid[12] are used sometimes. Depending on the solvent, the condensing agent, and the nature of the carbonyl and methylene components, the yields vary from 20 to 80%:

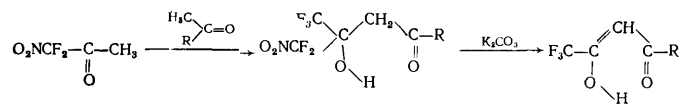


(I)

β-Diketones with a single fluorinated substituent have been obtained by this method: $R^F = CH_2F$,[12,15] CCl_2F,[16] CHF_2,[17] $CClF_2$,[18] CF_2OCF_3,[19,20] $CF_2\overline{CFCF_2CF_2CF_2}O$,[19,20] CF_3,[7,8] C_2F_4H,[21] C_2F_5,[18] C_3F_7,[22] C_4F_8H,[17] C_4F_9,[23] C_5F_{11},[24] C_7F_{15},[24,26] C_8F_{17},[27] C_6H_3XF (X = CH_3, Cl, OH, or CF_3),[9,10,28] $C_6H_4CF_3$,[29] or C_6F_5[11] (the second substituent is R = alkyl, aryl, or heteroaryl). Diketones with two fluorinated substituents have also been synthesised: $R^F = R = CF_3$,[7,15,30] HCF_2,[31] HC_2F_4,[31] C_7F_{15},[24,25] or C_6F_5;[11] $R^F = CH_3$, R = HCF_2,[31] C_2F_5,[32] C_3F_7,[32] C_7F_{15},[25] or

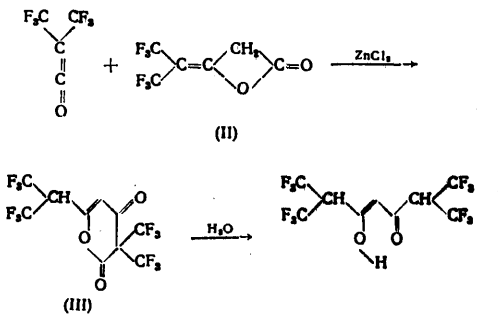


A number of other methods of synthesising polyfluorinated β-diketones are known. Knunyants and coworkers[34] described a synthesis of β-diketones containing the trifluoromethyl group; it is carried out by eliminating difluoronitromethane from β-hydroxyketones obtained by the condensation of pentafluoronitroacetone with methyl ketones:

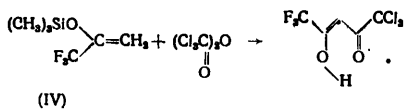


A novel method of synthesising 1,1,1,7,7,7-hexafluoro-2,6-bis(trifluoromethyl)heptane-3,5-dione in 70% yield has been patented; it consists in condensing bis(trifluoromethyl)keten with the β-lactone of 3-hydroxy-4,4-bis(trifluoromethyl)but-3-enoic acid (II) [acetyl chloride can be used instead of compound (II)] in the presence of zinc chloride and subsequent hydrolysis of the resulting δ-lactone of 5-hydroxy-2,2,6,6-tetrakis(trifluoromethyl)-3-oxohex-4-enoic acid

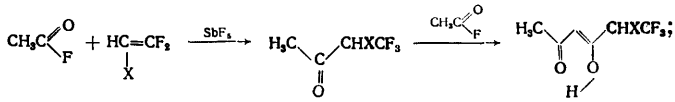
(III):[35]



Fokin and Uzun[36] showed that, when β-nitrotetrafluoroethyl nitrite reacts with acetone or acetophenone, up to 40% of the corresponding β-diketones (*I*, $R^F = CF_2NO_2$; $R = CH_3$ or C_6H_5) is formed. It has been established[37] that *O*-silyl-substituted enols (IV) are acetylated by the anhydrides of carboxylic halogenoacids at the terminal sp^2-hybridised carbon atom with formation of up to 43% of the corresponding β-diketone:

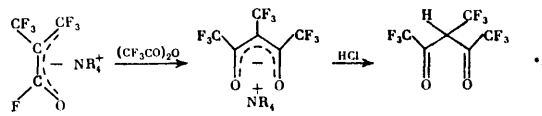


An interesting and promising method has been proposed[38] for the synthesis of β-diketones which are difficult to obtain, consisting in the interaction of fluoro-olefins with acid fluorides under pressure in the presence of antimony pentafluoride. The authors[38] suggest that a ketone is formed initially in the reaction and then reacts with the acid fluoride via a mechanism involving an acid-catalysed Claisen condensation:

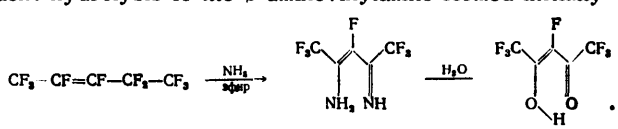


X = F or H.

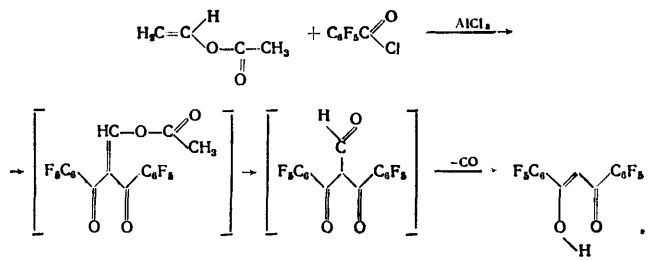
Knunyants and coworkers[39] succeeding in synthesising β-diketones with a fluorinated substituent in the α-position by treating mesomeric fluorocarbanions with the anhydrides of carboxylic perfluoroacids:



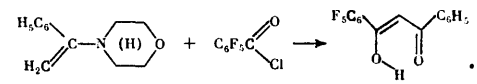
Heptafluoroacetylacetone has been synthesised recently by treating *trans*-perfluoropent-2-ene with ammonia and subsequent hydrolysis of the β-aminovinylimine formed initially[40]:



The use of the Claisen condensation[11,33] for the synthesis of β-diketones with pentafluorophenyl substituents frequently leads to the formation of chromones and flavones[41,42] owing to to ease of displacement of the *ortho*-fluorine atom from the pentafluorobenzoyl group by nucleophiles. A number of specific methods are therefore used for the synthesis of such diketones[11,42]. Thus Osadchii and Barkhash[42] synthesised decafluorodibenzoylmethane (DFBM), pentafluorodibenzoylmethane (PFDM), and 1,4-bis(pentafluorophenyl)butane-1,3-dione by acylating pentafluorobenzoylacetic ester with the chlorides of pentafluorobenzoic, benzoic, and pentafluorophenylacetic acids respectively and subsequent hydrolysis and decarboxylation under the influence of concentrated sulphuric acid. They were also the first to obtain perfluorodibenzoylmethane by fluorinating the sodium salt of DFBM with perchloryl fluoride[43]. Although DFBM is formed also when the dichloride of malonic acid is acted upon by pentafluorophenylcopper in absolute ether (yield 20%),[11] the difficulty of obtaining pentafluorophenylcopper and the low yield of DFBM limit the employment of this method. The same compound was synthesised by condensing pentafluorobenzoyl chloride with vinyl acetate in the presence of aluminium chloride (yield 34%):[11]



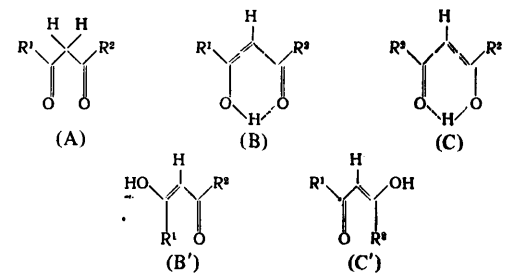
PFBM is obtained in 25% yield by the reaction of α-morpholinostyrene with pentafluorobenzoyl chloride in anhydrous dioxan[11]. The attempt to extend the method to the synthesis of DFBM proved unsuccessful.



In order to isolate and purify them, β-diketones are distilled[8,19,20] or converted into copper chelates, which are then recrystallised from organic solvents and decomposed with sulphuric acid[22] or hydrogen sulphide[7]. Vacuum sublimation is used to prepare high-purity chelates[25].

III. STRUCTURE AND ENOLISATION

β-Diketones constitute a prototropic system, which can exist in three tautomeric forms (A)–(C), for two of which [(B) and (C)] there is a possibility of geometrical *cis–trans* isomerism [(B') and (C')]. However, a number of studies have shown[44] that non-cyclic β-diketones exist only in the tautomeric forms (A)–(C).



The introduction of electron-accepting fluorine-containing groups greatly alters the distribution of electron density in the β-diketone molecule, which influences the keto–enol equilibrium. Indeed, a higher degree of enolisation of polyfluoro-β-diketones compared with the non-fluorinated compounds

was established as early as 1953 (with the aid of bromination) and infrared spectra have led to the hypothesis that they exist in the *cis*-forms (B)–(C) with an intramolecular hydrogen bond (IAHB).[23] Subsequently this hypothesis was confirmed by infrared spectroscopic[33,45–49], ultraviolet spectroscopic[33,45,50,51], and ^{1}H NMR [44,52,53] data.

The study of the ^{1}H NMR spectra of liquid β-diketones showed that the increase of the fluorine content shifts the keto–enol equilibrium towards the enol (Table 1) and that in the presence of four or more fluorine atoms in the molecule the enolisation is complete[12,17,20,54]. This agrees well with data for the enolisation of esters of fluorine-containing β-ketoacids[55] and is associated with the pronounced electron-accepting properties of the fluoroalkyl groups[46,56]. It is of interest that 1,1,1,5,5,5-hexafluoro-3-trifluoromethylpentane-2,4-dione, containing three CF_3 groups, is not enolised and exists fully in the diketo-form[39], although its non-fluorinated analogue is 30% enolised[57]. The influence of the solvent on the keto–enol equilibrium and on the chemical shifts of the protons of trifluoroacetylacetone (TFAA) and hexafluoroacetylacetone (HFAA) has been investigated[58].

Table 1. The contents of the enolic form in polyfluoro-β-diketones R^1–CO–CH_2–CO–R^2 according to ^{1}H NMR data for the pure liquids at 33–35 °C.

R^1	R^2	Content of enol, %	δ_{OH}, p.p.m.	Refs.
CH_3	CH_3	81	15.6	52
H_2CF	CH_3	87*	14.7	12
HCF_2	CH_3	95–97	17.6	17
CF_3	CH_3	97	14.1	54
HCF_2CF_2	CH_3	100	14.86	13
HCF_2	HCF_2	100	12.98	31
CF_3	CF_3	100	13.0	54

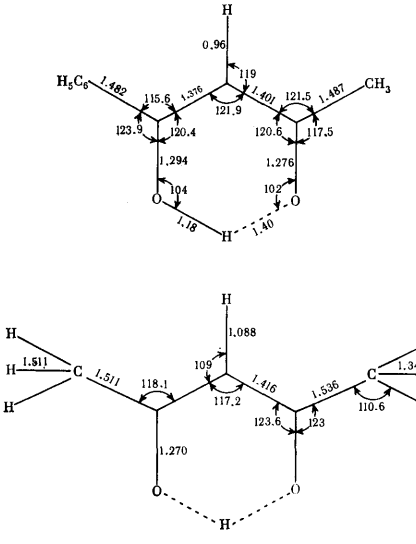
*At 26 °C.

The pronounced electron-accepting properties of fluoroalkyl substituents are also manifested by the weakening of the IAHB in fluorine-containing β-diketones compared with the non-fluorinated compounds. Thus it has been established[59] that the signal of the O–H proton is displaced upfield on passing from acetylacetone (AA) to TFAA and HFAA and also from benzoylacetone (BA) to trifluorobenzoylacetone (TFBA); according to the authors[59], this demonstrates a weakening of the IAHB. An analogous relation has been found[60] for β-diketones of the selenophen series. On the basis of HFAA as an example, Gunnarsson et al.[61] suggest that the strength of the IAHB be estimated from the correlation between the proton chemical shifts and the isotope effect on replacement of the OH proton by deuterium for the same hydrogen-bonded systems; however, studies of this kind have not been carried on fluorine-containing β-diketones.

Asymmetric polyfluoro-β-diketones with a fluoroalkyl substituent at only one carbonyl group are convenient objects for the investigation of the position of the proton in the *cis*-enol form with an IAHB (a study of the enol–enol equilibrium), but here too the studies which have been carried out are restricted mainly to the non-fluorinated dicarbonyl compounds. Thus, analysis of the chemical shifts of the enol protons in the ^{1}H NMR spectra of *para*-substituted BA led to the conclusion[62] that the fraction of the enolic form with the proton at the oxygen atom linked to the benzene ring increases as the electron-accepting properties of the *para*-substituent in the ring are enhanced. This is also confirmed by data[63] where an analogous conclusion concerning the preferred mode of enolisation of β-diketones involving the oxygen atom linked to the more electron-accepting substituents was reached on the basis of a study of ^{17}O NMR. This mode of enolisation was confirmed elegantly for asymmetrical polyfluoro-β-diketones by the results of a study[64] in which the influence of the solvent on the chemical shifts of the carbon nuclei of both carbonyl groups in AA, dibenzoylmethane (DBM), TFAA, and salicylaldehyde was investigated by ^{13}C NMR; it was established that in TFAA the carbonyl group linked to the trifluoromethyl group is enolised.

On the basis of the study of the ^{13}C NMR spectra of the enolic forms of fluorine-containing and hydrocarbon β-diketones, it was concluded that they do not undergo the enol–enol tautomerism and the observed changes in the chemical shifts of the carbon nuclei were explained by a redistribution of the electron density in the chelate ring with an IAHB.[65] Nevertheless the same investigators[66] proposed a method for determining the position of the proton in the chelate with an IAHB from the ^{13}C NMR spectra of metal chelates; the presence of two equivalent potential wells for the bridging hydrogen atom in HFAA was pointed out in an earlier study[67].

The recently observed simultaneous presence of the enolic and enthiol forms in solutions of fluorine-containing monothio-β-diketones cooled to −70 °C constitutes a convincing confirmation of the occurrence of intrachelate tautomerism in β-diketones[68].



The bond lengths (in Å) and angles (in degrees) in BA [71] and TFAA [69] molecules.

Molecular Structure

The determination of the molecular geometries of the enolic forms of TFAA [69] and HFAA [70] by electron diffraction in the gas phase and X-ray diffraction study of the crystal and

molecular structures of BA,[71] *p*-nitrobenzoylacetone[72], and DBM [73] also failed to provide an unambiguous answer to the question of the position of the proton in the enolic tautomers (see Figure). According to Andreassen and coworkers[69,70], the experimental distances between the two oxygen atoms are in best agreement with the symmetrical form (an analogous conclusion was reached by Jones[72]); on the other hand, an asymmetric structure of BA and DBM molecules was indicated in other investigations[71,73].

Two O(1) ionisation bands, differing by 1.5 eV, were recently found by photoelectron X-ray spectroscopy and it was established that AA and HFAA exist in two tautomeric forms (B) and (C), the barrier to their interconversion via the enolic form with a symmetrical location of the proton being low.[74] For HFAA, this conclusion was confirmed[61] by a study of the ^1H NMR and ^2H NMR spectra.

Distribution of Electron Density

The distribution of electron density in the enolic forms of polyfluoro-β-diketones has been calculated by the CNDO method[75-77]. An increased electron density at the carbon atom linked to the fluorinated substituents has been observed for TFAA.[75,76] The study of the influence of the structure of the fluoroalkyl substituent on the distribution of electron density showed[77] that the distribution depends little on the position of the proton in the enolic forms of β-diketones.

Table 2. The ionisation constants of polyfluoro-β-diketones $R^1-CO-CH_2-CO-R^2$.

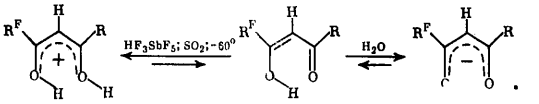
R^1	R^2	pK_a	Solvent	Temp., °C	Refs.
CH_3	CH_3	9.05±0.04	5% aqueous ethanol	20	31
CH_3	CF_2H	7.07±0.09	ditto	20	31
CH_3	CF_3	6.56±0.09	»	20	31
CH_3	CF_2CF_2H	5.51±0.09	»	20	31
CH_3	CF_2CF_3	5.17±0.02	»	20	31
CH_3	$(CF_2)_4H$	4.7±0.10	»	20	31
CF_2H	CF_2H	5.37±0.06	»	20	31
CF_3	CF_3	4.6	water	25	84
CF_3	CF_3	5.3	»	25	85
CF_3	CF_3	6.0	75% aq. dioxan	25	79
CF_2CF_2H	CF_2CF_2H	2.43±0.07	5% aq. ethanol	20	31
	CF_3	6.35±0.03	80% aq. methanol	25	20
ditto	CF_2OCF_3	6.22±0.03	ditto	25	20
»		4.95±0.70	»	25	20

IV. ACID–BASE PROPERTIES

Depending on the acidity of the medium, β-diketones exhibit the properties of acids or bases, splitting off or combining with a proton. In aqueous media polyfluoroalkyl-β-diketones are stronger acids by 2–3 orders of magnitude than the corresponding non-fluorinated analogues. This was demonstrated by the determination of their ionisation constants in a series of aqueous organic systems (50% dioxan–water[78], 75% dioxan–water,[79,80] 46% acetone–water,[81] 80% methanol–water,[20] 5% ethanol–water,[31] and dimethylformamide [82]) and in water[83-85] and are clearly illustrated by measurements[85] of the pK_a of *m*- and *p*-substituted benzoyltrifluoroacetones.

The influence of the structure of the fluorinated substituent on the acid dissociation constants of polyfluoro-β-diketones in solutions are illustrated in Table 2. However, even the lowest of the available literature values of pK_a for HFAA, which is 4.6,[84] is in poor agreement with the pK_a of other β-diketones and in all probability characterises the acidity of the dihydrate of hexafluoroacetyl-1,1,1,5,5,5-hexafluoropentane-2,2,4,4-tetraol which is formed extremely readily when HFAA comes into contact with water (see Section V).[31] A linear relation has been found between pK_a and the Taft σ* constants of the substituents R for constant R^F, which is not observed when R^F is varied and R is kept constant; it was established that the acidity of polyfluoro-β-diketones increases with the chain length of R^F from CF_3 to $(CF_2)_4H$.

In weakly acid solutions non-fluorinated β-diketones form both monocations (96% H_2SO_4) and dications ($HFSbF_5$ in SO_2);[86,87] polyfluoroalkyl-β-diketones undergo monoprotonation under the same conditions[87,88]:



The basicity constant pK_b of thenoyltrifluoroacetone (TTFA) in sulphuric acid proved to be −5.2 in a spectrophotometric determination and −5.3 in a potentiometric determination[89].

V. CHEMICAL REACTIONS

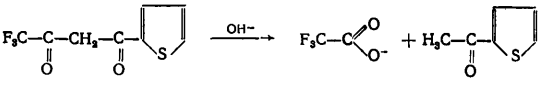
1. Reactions of Carbonyl Groups

Most of the synthetic studies on polyfluoro-β-diketones are associated with the investigation of the reactions of carbonyl groups with nucleophiles, since these reactions in fact open the way to different β-diketone derivatives and make it possible to obtain a wide range of compounds, including aza-heterocycles, with fluorine-containing substituents in the heteroring, many of which exhibit a high biological activity.

(a) Interaction with hydroxy-compounds.

The interaction of polyfluoro-β-diketones with hydroxyl-containing nucleophiles (water and alcohols) has been little studied, although it is of interest, because β-diketones are used fairly widely as extractants of metal cations from aqueous media[90].

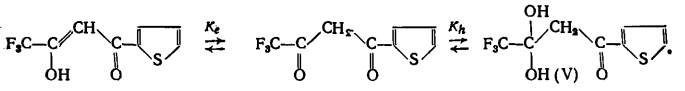
In an alkaline medium polyfluoro-β-diketones are cleaved like their hydrocarbon analogues[91] and diketones with a single polyfluoroalkyl substituent form a salt of a carboxylic polyfluoroacid and a methyl ketone[92]:



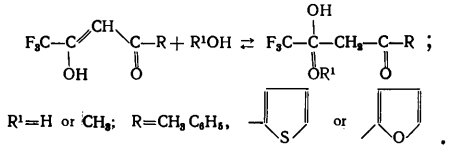
This shows that the nucleophilic attack is directed to the carbonyl linked to the fluorinated substituent. The replacement of one of the fluorine atoms of the trifluoromethyl group by the nitro-group facilitates hydrolytic cleavage still further and 1,1-difluoro-1-nitropentanedione is cleaved on being simply boiled with water[36].

Nevertheless asymmetric polyfluoro-β-diketones without NO_2 groups in the molecule are not hydrolysed under the usual condition in an acid or neutral medium and, like other halogen-containing carbonyl compounds[94], form geminal

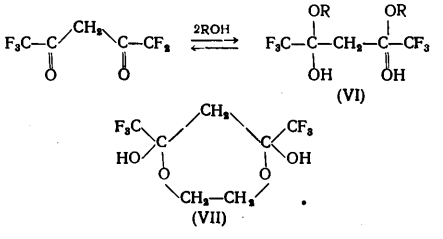
adducts. Thus, when TTFA was dissolved in the benzene–water two-phase system, it was observed[95] that the diketone in benzene solution is hydrated to a large extent (12%). These data are confirmed by the anomalously low (2%) content of the enolic form of TTFA in aqueous solution, which has been attributed[96] to the formation of the hydrate (V), which shifts the diketone–enol equilibrium towards the diketo-form and further towards the hydrate:



In a series of studies[97–99] investigation of the NMR ^{19} and ^{1}H NMR spectra of a series of trifluoromethyl-β-diketones showed that water or an alcohol adds reversibly to one of the carbonyl groups. The equilibrium constants and the heats of formation of the adducts have been determined. From the study of the equilibrium between the initial forms of the trifluoroacetoacetic ester (the keto- and enolic forms), on the one hand, and the corresponding hydrates and hemiketals, on the other, it was concluded that water interacts exclusively with the keto-form[100]. The rate of this interaction exceeds the rate of the keto–enol transformation. It has been shown[101] that the tendency of fluorine-containing β-diketones to form geminal adducts diminishes when one CF_3 group in HFAA is replaced by the α-thienyl (TTFA), phenyl (BTFA), or methyl (TFAA) groups:



In the case of HFAA, which contains two trifluoromethyl groups, water or alcohol adds to both carbonyl groups and the resulting geminal adducts (IV) (tetraols and bishemiketals) are so stable that they can be isolated in a free form[30,102,103]. The reaction of HFAA with ethylene glycol leads to 5,7-dihydroxy-5,7-bis(trifluoromethyl)dioxepan (VII):[104]

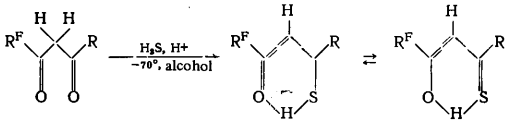


The equilibrium in the reaction of HFAA with water is strongly displaced towards the adduct, while in ethereal solution only an insignificant amount of the enolic form is present[30] and the abstraction of both water molecules requires prolonged refluxing over P_2O_5.

It is of interest that an increase in the length of even one of the two fluoroalkyl substituents in β-diketones (analogues of HFAA) reduces sharply the stability of the dihydrates. For example, the crystalline adducts of water with a diketone incorporating CF_3 and C_3F_7 groups, namely 1,1,1,5,5,6,6,7,7-decafluoroheptane-2,4-dione is stable only at −25 °C, decomposing on heating to room temperature with elimination of water[32], although the similar adduct of a β-diketone containing the CF_3 and C_2F_5 groups is entirely stable. On the other hand, a stable dihydrate is formed when one trifluoromethyl group is retained in the molecule, while the other is replaced by the difluoromethyl-containing group $-HCF_2-C(OH)_2-CH_2-C(OH)_2-CF_3$.[31]

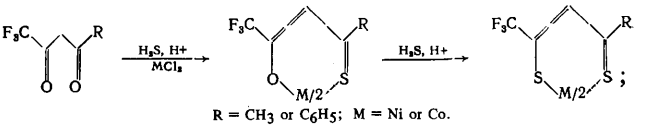
(b) Interaction with hydrogen sulphide.

The interaction of β-diketones with hydrogen sulphide in the presence of basic[105,106] or acid[107,108] catalysts leads to the replacement of one or both oxygen atoms in the carbonyl groups by sulphur. The study of this reaction in relation to polyfluoro-β-diketones demonstrated the necessity to increase the concentration of the catalyst (anhydrous hydrogen chloride) as the electron-accepting properties of the substituents at the carbonyl groups are enhanced, which can be accounted for[108] by the necessity to displace the keto–enol equilibrium towards the reactive diketo-form. A series of monothio-β-diketones with different fluoroalkyl (CF_3,[108–113] HCF_2CF_2,[114] C_2F_5,[110,113] and C_3F_7 [113,115]) and hydrocarbon groups have now been obtained by this method:



It has been shown by mass spectrometry that the condensation involves the carbonyl group linked to the least electron-accepting substituent[108,116]. On this basis, it is suggested[117] that the attacking species in the reaction of β-diketones with hydrogen sulphide is H_3S^+ and the reaction is electrophilic. The mechanism involving the protonation of the carbonyl group and nucleophilic attack by hydrogen sulphide is more probable[118].

The replacement of the oxygen of the second carbonyl group by sulphur with formation of dithio-β-diketones is possible, but these compounds are relatively unstable and readily dimerise[119,120]. The attempts to synthesise dithiohexafluoroacetylacetone and its chelates proved unsuccessful[121,122]. Only the synthesis and spectroscopic study of the nickel and cobalt chelates of dithiotrifluoroacetylacetone and dithiodifluorobenzoylacetone when hydrogen sulphide is passed into concentrated solutions of β-diketones and salts of the corresponding metals in absolute alcohol saturated with hydrogen chloride has been reported; the yields amount to 15–30%. The reaction mechanism proposed by Barraclough et al.[122] involves the formation of a monothio-β-diketone, which is then coordinated to the metal, so that the subsequent introduction of sulphur takes place, as it were, on a matrix. In all probability this reaction is possible by virtue of the presence of hydrogen chloride, which prevents the formation of the metal sulphide and the reversible decomposition of the metal chelate by hydrogen sulphide:

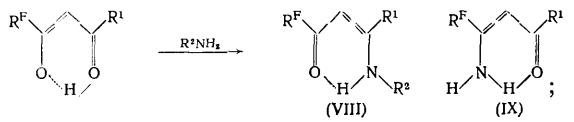


(c) Reactions with amino-compounds

The interaction of polyfluoro-β-diketones with an amine can involve one or both carbonyl groups of the β-diketone molecule (and sometimes also the α-carbon atom), depending on the nature of the amine, the reaction conditions, and the

structure of the substituents at the carbonyl groups, with formation of β-aminovinyl ketones (β-AVK), as well as various saturated or aromatic heterocycles.

Reactions with ammonia and primary amines. When solutions of polyfluoro-β-diketones are refluxed with ammonia or primary amines under the conditions of acid catalysis or in the absence of a catalyst, β-AVK (VIII) are formed[29,123–127] and, in the case of asymmetric β-diketones with a single fluoroalkyl substituent, the carbonyl group linked to the non-fluorinated substituent is involved in condensation. This has been established by the synthesis of isomeric β-AVK (IX) with the amino-group at the fluoroalkyl substituent[128] and has been confirmed mass-spectrometrically[127]:



(VIII) (IX)

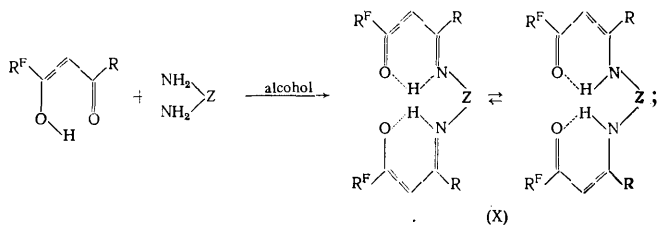
R^F=CF_3[123], HCF_2[127], H $(CF_2)_2$[126,127], H $(CF_2)_4$[127],

$CF_3C_6H_4$[29]; R^1 — alkyl, fluoroalkyl, or aryl; R^2—H, alkyl, aryl, or $N{=}C(CF_3)_2$

The analogous reactions of the esters of fluorine-containing β-ketoacids involve the ketone carbonyl group linked to the fluorinated substituent[129,130].

The condensation of both carbonyl groups in polyfluoro-β-diketones with free monoamines, leading to the formation of fluorine-containing β-di-imines, is unknown, but treatment of an alkaline solution of TFAA with platinum hexammine gave a β-di-imineplatinum complex in 40% yield[131,132]. According to the authors[131,132], the reaction constitutes a promising method for the synthesis of β-aminovinylketimines, but they did not describe the isolation of the ligand in a free form. In our view the interaction of perfluoro-olefins with ammonia may serve as a simpler and more reliable method of synthesising fluorine-containing β-aminovinylketimines[40].

In the interaction of polyfluoro-β-diketones with polyalkylenepolyamines one carbonyl group from each two diketone molecules and both terminal amino-groups of the polyalkylenepolyamine are as a rule involved in condensation; this leads to high yields of the corresponding bis(β-dioxo)-alkylenedi-imines (X):[133–140]



(X)

Z=CH_2CH_2[133,134,136,138], $CH_2CH(CH_3)$[134],

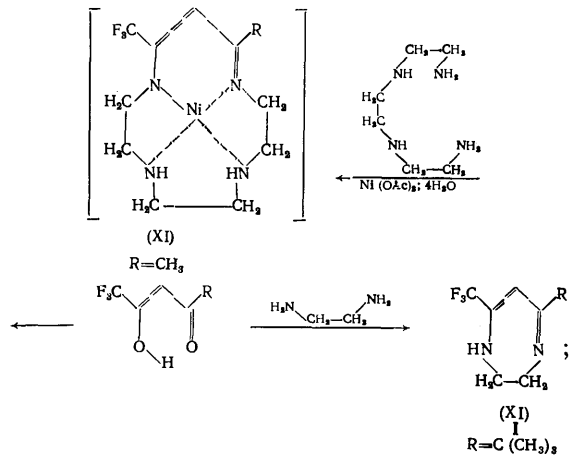
$CH_2CH_2CH_2$[135,136,138], $CH_3CHCHCH_3$[137],

$(CH_2)_2NH(CH_2)_2NH(CH_2)_2$[139], or $(CH_2)_2NH(CH_2)$—$_2$[140].

Recently there has been a growth of interest in these compounds in view of the discovery of their properties satisfying many of the requirements of the metal chelate gas chromatography[136–138]. The monomeric structure of bis(β-dioxo)alkylenedi-imines has been confirmed by the determination of their molecular weights[139] and by the formation of individual metal chelates[134,137,138]. The direction of nucleophilic attack in the case of asymmetric β-diketones on the carbonyl linked to the non-fluorinated substituent has been established by determining the dipole moments[134,135] and by the mass-spectrometry[93,141] of the compounds themselves, as well as the X-ray diffraction analysis of their nickel(II) chelates[142]. On the basis of this direction of attack, it is suggested that the electron-accepting CF_3 group induces a larger δ+ charge on the remote carbonyl than on the carbonyl linked to this group[142].

The question of the tautomeric structure of the compounds remains controversial: some workers[134,135] are inclined towards the iminoenol structure, while in other investigations[93,139] preference is given to the enaminoketone form on the basis of the ^1H NMR spectra and dipole moments, which appears to be more correct.

Only isolated instances of the formation of cyclic compounds in this reaction have been described. Thus the reaction of TFAA with triethylenetetramine in the presence of nickel ions yielded compound (XI),[143] and the synthesis of dihydrodiazepine (XII) has been reported[144]:



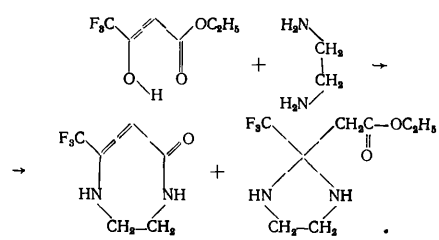
(XI)

R=CH_3

(XI)

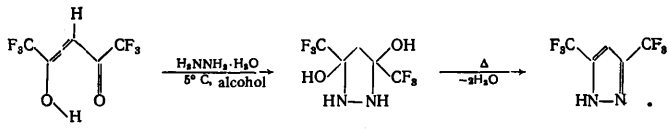
R=$C(CH_3)_3$.

Depending on the conditions, the condensation of the esters of fluorine-containing β-ketoacids with ethylenediamine leads either to a mixture of a substituted 2,3-dihydro-1,4-diazepin-5-one and imidazolidine in various proportions or to the imidazolidine alone[129,145]:



Reactions with hydrazines and hydroxylamine. Like their hydrocarbon analogues[146], polyfluoro-β-diketones react with hydrazines at room temperature[147] or on heating to form pyrazoles[93,148–153], among which compounds with anti-inflammatory and analgesic activities[147,148], highly active herbicides[150], preparations for the treatment of hyperglycemia[152], heat resistant heat exchanger, and surfactants[153] have been patented. Interaction of bis-β-diketones with hydrazines proceeds similarly and leads to bispyrazoles[93].

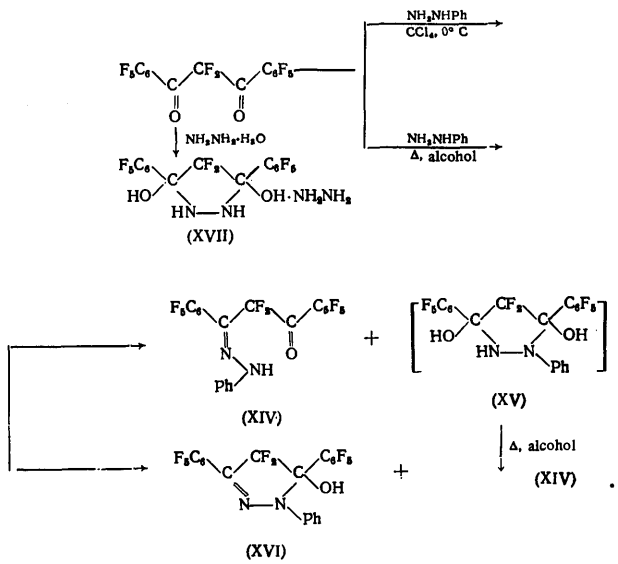
In contrast to this, the interaction of HFAA with hydrazine hydrate in alcohol (5 °C) gives rise to 3,5-dihydroxy-3,5-bis(trifluoromethyl)pyrazolidine (XIII),[154] which splits off two water molecules only on heating and is converted into pyrazole:



(XIII)

For symmetrical polyfluoro-β-diketones with large aliphatic fluorosubstituents [153] and with fluorinated substituents containing an ω-hydrogen atom[93], the formation of pyrazolidines was not observed at all in this reaction; this is consistent with the reactivity of symmetrical polyfluoro-β-diketones in relation to hydroxylated nucleophiles.

The behaviour of β-diketones with perfluorophenyl substituents in reactions with hydrazines is unusual; perfluorodibenzoylmethane, which has no α-hydrogen atom, reacts with phenylhydrazine at 0 °C to give a mixture of the β-ketohydrazone (XIV) and the unstable pyrazolidine (XV), the refluxing of which in alcohol results in the elimination of one water molecule and the formation of the pyrazoline (XVI), together with the partial opening of the ring and conversion into compound (XIV).[155] The reaction with hydrazine hydrate yields the pyrazolidine (XVII) as an adduct with a hydrazine molecule:



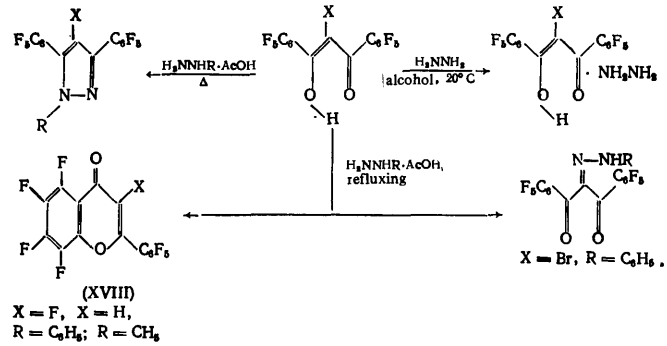
(XVII)

(XIV)

(XV)

(XVI)

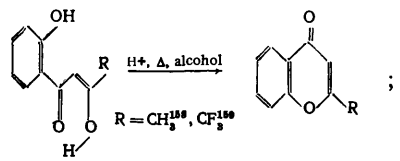
The enolising aromatic polyfluoro-β-diketones react with hydrazine at room temperature to form salts, pyrazoles being produced only on boiling. However, depending on the nature of the α-substituent in the β-diketone and the structure of the hydrazine, on heating with hydrazine acetates they form either pyrazoles or the flavones (XVIII) via the intramolecular elimination of an *ortho*-fluorine atom from the pentafluorophenyl ring[156]:



(XVIII)

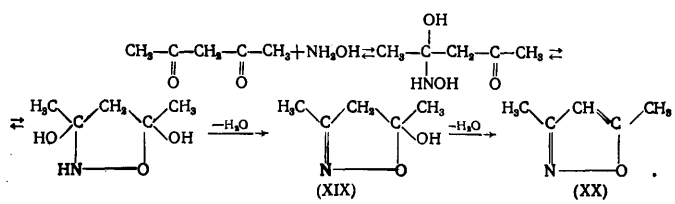
X = F, X = H,
R = C_6H_5; R = CH_3

A similar reaction, leading to the formation of flavones by the intramolecular cyclisation of β-diketones with a non-fluorinated phenyl substituent, occurs only on heating in the presence of an inorganic acid and requires the obligatory presence of a hydroxy-group in the *ortho*-position in the benzene ring[157,158]:



Recent studies of the reaction mechanism by NMR in relation to AA have shown that the interaction of β-diketones with hydroxylamine involves several stages and ultimately leads to isoxazoles (XX).[159,160]

In the case of polyfluoro-β-diketones the intermediate 5-hydroxy-Δ^2-isoazoline of type (XIX) is so stable that it can be isolated in a free form and its conversion into isoxazole requires heating with polyphosphoric acid[161,162]. This demonstrates yet again the stabilisation of the intermediates of the nucleophilic addition reaction by fluoroalkyl residues:

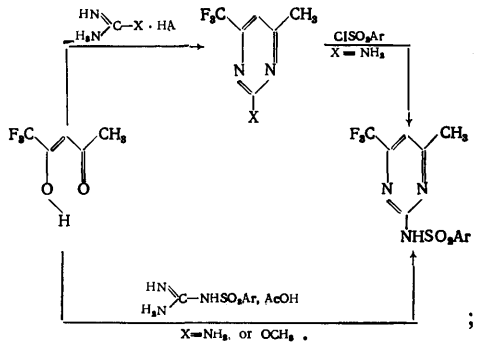


(XIX) (XX)

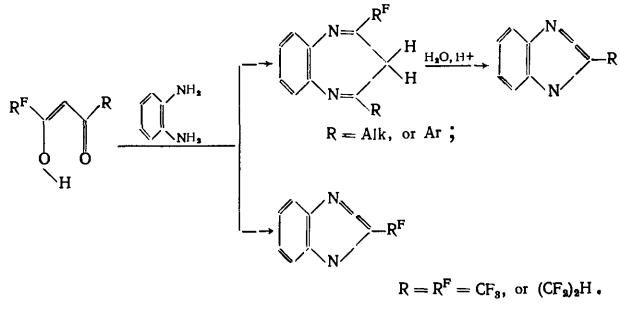
Fluoroalkylisoxazoles have been patented as high-temperature heat exchangers and surfactants[161] and also as substances reducing the sugar content in blood[163].

Reactions with urea derivatives and o-phenylenediamine. When TFAA is fused together with guanidine carbonate[149] and on heating alcoholic solutions of TFAA with guanidine carbonate[164] or *O*-methylisourea hydrochloride[175], 2-amino- or 2-hydroxy-pyrimidines with the trifluoromethyl group in the heteroring are formed, among which trifluoromethylsulphonamides—the analogues of the familiar non-fluorinated preparation sulphamethazine and sulphisoamidine—have been obtained[164]. The synthesis of these compounds in a single

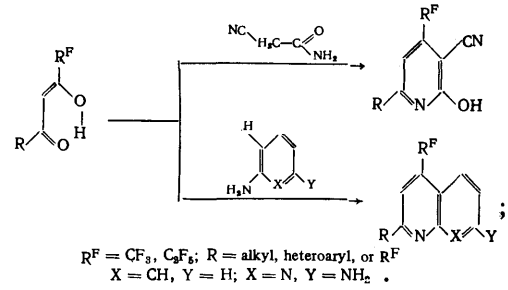
stage by refluxing TFAA with arenesulphonylguanidines has been patented[166]. The same patent reports their higher biological activity compared with the hydrocarbon analogues. It has been shown[167] that in an acid medium the reaction mechanism involves the acid-catalysed attack by urea on the keto–enol with subsequent cyclisation:



Although the formation of substituted 1,5-benzodiazepines from o-phenylenediamine (OPD) and β-diketones without fluorine was described as early as 1907,[168] the study of the interaction of fluorine-containing β-diketones with OPD was begun only in recent years. It has been established[169] that the condensation of fluoroalkyl-β-diketones with OPD results in the formation of between 3 and 25% of the open-chain β-aminovinyl ketone, depending on the substituents in the β-diketone, together with 1,5-benzodiazepines. It is recommended that the 1,5-benzodiazepines with a fluoroalkyl substituent in the heteroring obtained in this reaction be used as surfactants and heat exchangers[170]. It has been observed[93] that benzodiazepines can be obtained successfully only from β-diketones containing a single fluoroalkyl substituent, while β-diketones with two fluoroalkyl substituents give rise to salts under the usual conditions of condensation with OPD,[168] refluxing in alcohol in the presence of acetic acid producing 2-fluoroalkylbenzimidazoles[93]. This course of the reaction is associated in all probability with the enhanced reactivity of the C=N bond adjoining the fluoroalkyl substituent, which leads to attack by the free amino-group on this bond and not on the carbonyl group:



Reactions with amino-compounds containing mobile α-hydrogen atoms. Under the influence of basic reagents[171,172], sulphur[173], polyphosphoric acid[174,175] phosphoric acid[176–178], and also on heating[179], polyfluoro-β-diketones readily condense with amino-compounds containing a mobile hydrogen atom in the β-position with formation of a pyridine ring:

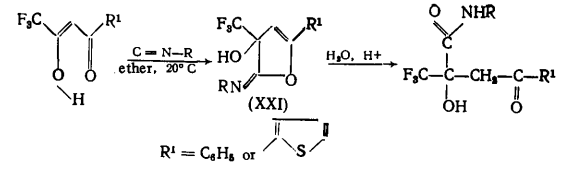


The reaction is of interest from the standpoint of the introduction of fluorine-containing substituents into the pyridine ring and the synthesis of potential biologically active compounds. Thus the substituted 4-trifluoromethylpyridone, synthesised from cyanoacetamide and TFAA, has been used to prepare trifluoromethyl analogues of vitamin B_6,[171] pyrazolopyridines with a 4-fluorophenyl substituent have been patented as anti-inflammatory preparations[174], and the naphthyridines obtained from fluorine-containing β-diketones and 2,6-diaminopyridine have been patented as compounds with hypotensive and bronchodilating activities[175,177,178]. The analogous cyclisation with esters of fluorine-containing β-ketoacids leads to γ-pyridones[180], from which trifluoromethyl analogues of quinine and quinidine have been obtained. The formation of trifluoromethylpyrazolo[1,5-d]pyrimidines by the condensation of TFAA with 2-aminopyrimidine has been described[181]. The compounds obtained are depressants of the central nervous system.

(d) Reactions with other nucleophiles

Selenothenoyltrifluoroacetone has been obtained by the reaction of an alcoholic solution of TTFA with hydrogen selenide in a stream of nitrogen in the presence of anhydrous hydrogen chloride[182]. The site of nucleophilic attack has not been established, but, by analogy with hydrogen sulphide[108], it has been suggested[182] that the oxygen of the carbonyl group linked to the non-fluorinated substituent is substituted (see also Section V).

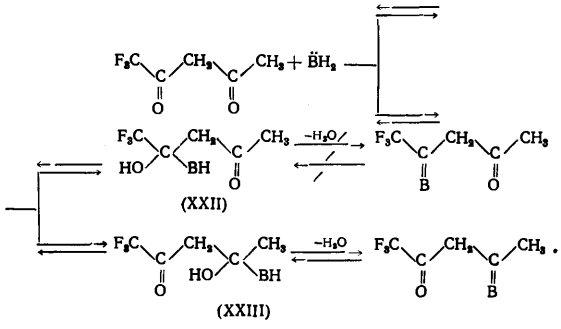
In contrast to their non-fluorinated analogues[183], fluoroalkyl-β-diketones readily give rise to cyclicadducts with isonitriles in the absence of catalysts[184], which is attributed to their virtually complete enolisation. The structure of the reaction product (XXI) and hence the direction of nucleophilic attack† on the carbonyl linked to the fluoroalkyl substituent have been established by ^{19}F NMR and the acid hydrolysis of the cyclicadduct:



† The authors[184] do not rule out the possibility of 1,4-cycloaddition.

The interaction of fluorine-containing β-diketones with the hydride ion leads to the reduction of both the carbonyl group and of the C=C double bond of the enol with formation of diols[185].

Thus polyfluoro-β-diketones readily react with nucleophiles, forming geminal adducts or condensation products. The unusual direction of nucleophilic attack on the carbonyl carbon atom linked to the less electron-accepting substituent can be accounted for either by the initial protonation of the carbonyl group linked to the non-fluorinated substituent or by treating the reaction as a series of reversible stages involving intermediate and final products[127]:



(XXII)

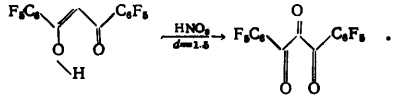
(XXIII)

The formation of the adduct (XXII) is more likely than that of the adduct (XXIII), but the former does not tend to eliminate a group and the reaction virtually stops at the stage involving its formation. The adduct (XXIII) readily eliminates either the added nucleophile molecule, being reconverted into the initial β-diketone, or a water molecule, forming a condensation product; in the presence of a large excess of the reagent, the equilibrium is displaced towards the condensation product. In an alkaline medium, the β-diketone molecule is cleaved irreversibly at the C–C bond.

2. Other Reactions

(a) Electrophilic reactions

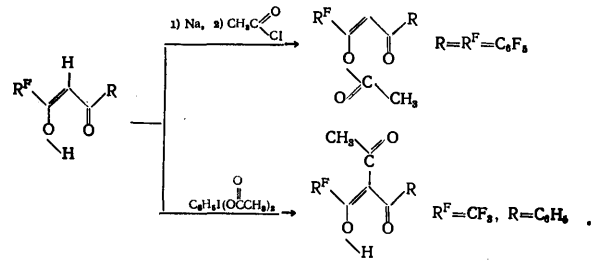
The interaction of fluorine-containing β-diketones with electrophiles has been studied less thoroughly than the interaction with nucleophiles, probably owing to the smaller practical and synthetic importance of the compounds formed. However, the available data emphasise certain features due to the presence of fluorine-containing substituents. For example, under conditions characteristic of the introduction of the nitro-group in the α-position of DBM, the fluorinated analogue of the latter is not nitrated and treatment with more concentrated HNO_3 results in the formation of a triketone, which is entirely stable in air[42]:



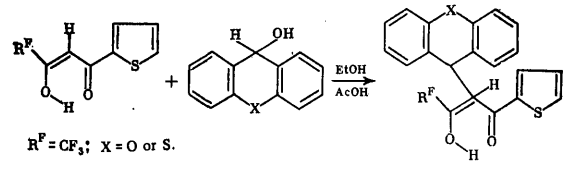
An analogous reaction has been observed for pentafluorobenzoylacetic ester on treatment with selenium dioxide[186].

Fluorine-containing substituents also hinder the bromination and nitration of chromium and copper β-diketonates. This is associated both with the reduction of the nucleophilicity of the α-position and with the decrease of the stability of the metal chelates themselves[187,188].

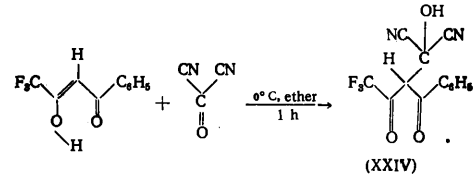
The dual reactivity of fluorine-containing β-diketones and their enolate ions has been very little investigated. It has been established that treatment of the sodium salt of DFBM with acetyl chloride results in the exclusive formation of the *O*-acetyl derivative[43]. The interaction of BTFA with diacetoxyiodobenzene leads to C-acylation[189]:



Alkylation of TTFA with xanthydrol and thioxanthydrol in acetic acid takes place at the α-carbon atom[190] and does not differ from the similar reaction of the non-fluorinated analogues:

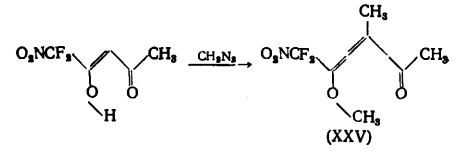


O-Alkylation also does not occur on interaction of TFBA with carbonyl cyanide, the relatively unstable C-alkylation product (XXIV) being formed in quantitative yields[191]:



(XXIV)

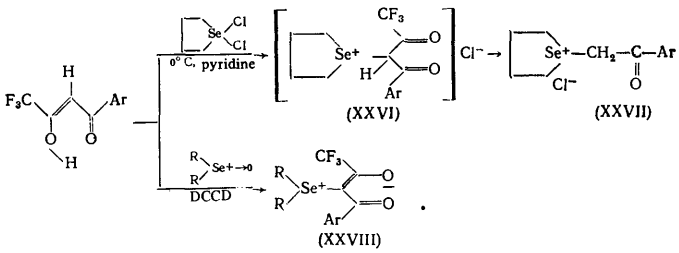
On the other hand, 1,1-difluoro-1-nitropentane-2,4-dione is methylated by diazomethane at the oxygen and α-carbon atoms, being converted into 5,5-difluoro-4-methoxy-3-methyl-5-nitropent-3-en-2-one (XXV);[36] this is yet another example of the dual reactivity of fluorine-containing β-diketones:



(XXV)

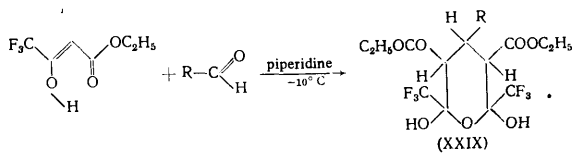
The attempt to extend to fluorine-containing β-diketones the reaction leading to the formation of selenonium ylids by treatment with selenolane dichlorides, which is usual for the non-fluorinated analogues, led to the selenonium salts (XXVII).[192] According to the authors, this is associated with the cleavage of the selenonium derivative of the diketone (XXVI) formed initially. The instability of the latter is

caused by the high positive charge on the carbonyl carbon atom linked to the trifluoromethyl group due to the inductive effect of the CF_3 and $>Se^+$ groups. The selenonium ylids (XXVIII) have been obtained only from selenoxides and the benzoyl- and thenoyl-trifluoroacetone in the presence of dicyclohexylcarbodi-imide (DCCD):[192]



(XXVI) (XXVII) (XXVIII)

The condensation of the α-methylene group of fluorinated β-diketones with polymethine compounds containing a terminal aldehyde group has been described; the products have been patented as filtering dyes for photographic and textile materials[193]. The condensation of the trifluoroacetoacetic ester with aqueous solutions of aldehydes leads to the tetrahydropyrans (XXIX) containing fluoroalkyl substituents in the heteroring[194]:

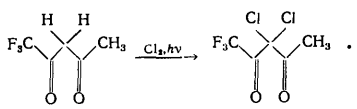


(XXIX)

Heating of TFAA with thionyl chloride leads to the substitution of the hydroxy-group by chlorine with formation of 2-chloro-1,1,1,5,5,5-hexafluoropentan-1-one.[195,196]

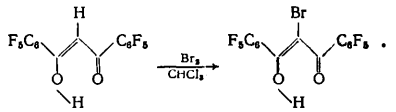
(b) Radical reactions

There have been several examples of radical reactions of fluorine-containing β-diketones. Chlorination of TFAA in the light leads to 3,3-dichloro-1,1,1-trifluoropentane-2,4-dione (XXX):[23]

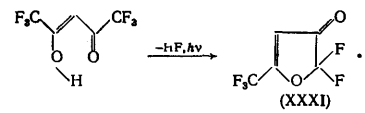


(XXX)

The bromination of DFBM with bromine results in the formation of only the monobromo-derivative, although under the same conditions the non-fluorinated analogue can give rise to both mono- and di-bromo-derivatives[42]:



It has been shown by EPR that trifluoronitrosomethane adds to TFAA and HFAA in the α-position with formation of nitroxy- and iminoxy-radicals[197]. Irradiation of HFAA with ultraviolet light leads to the elimination of HF and to cyclisation to 2,2-difluoro-5-trifluoromethyl-2,3-dihydro-3-furanone (XXXI):[198]

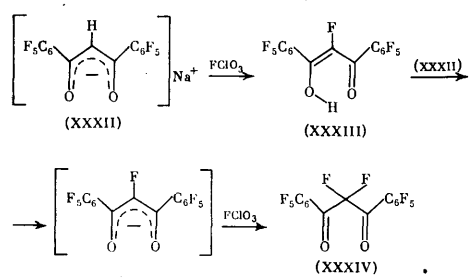


(XXXI)

в) Фторирование

(c) Fluorination

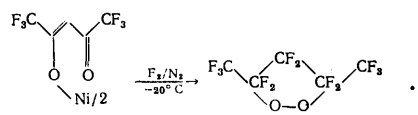
It has been shown[43] that the sodium salt of DFBM (XXXII) is fluorinated by perchloryl fluoride at the α-carbon atom with formation of perfluorodibenzoylmethane (XXXIV), which is consistent with data[199–201] for the interaction of non-fluorinated β-diketones with perchloryl fluoride and can be accounted for[43,199] by the higher acidity of the diketone (XXXIII) compared with DFBM, leading to its metallation by the sodium salt (XXXII) and further exhaustive fluorination:



(XXXII) (XXXIII) (XXXIV)

The introduction of only one fluorine atom at the α-carbon atom has been achieved[43] by fluorinating α-bromodecafluorodibenzoylmethane with subsequent debromination and also by fluorinating the sodium salt of bis(pentafluorobenzyl)acetic ester, and the acid cleavage of the resulting product with 100% sulphuric acid. The possible mechanism of the fluorination of CH-active compounds by perchloryl fluoride has been discussed in a book[202].

Fluorination with elemental fluorine has been described only for the copper and nickel chelates of hexafluoroacetylacetone; the authors were able to isolate perfluoro-3,5-dimethyl-1,2-dioxolan in 5% yield:[203]



VI. APPLICATIONS

1. Extraction and Extraction-Photometric Determination of Metals

The presence of fluorine-containing groups is reflected also in the applications of β-diketones, giving rise to new fields of application of these compounds or improving the properties for employment in familiar fields.

Thus the acidity of polyfluoro-β-diketones exceeds by 2–3 orders of magnitude the acidity of their non-fluorinated analogues[204,205], which permits the extraction of readily hydrolysable metal β-diketonates from much more acid solutions[90]. The studies on the extraction properties of TTFA and furoyltrifluoroacetone, which have been investigated in greatest detail in this sense, have been reviewed in a monograph[90] and the synergism of TTFA in combination with various compounds has been discussed in a review[206].

In publications of recent years much attention is devoted to the study of the extraction of metals with TTFA in the presence of tertiary amines[207-214] and phosphorus compounds[215-217] and also to the application of TTFA in the extraction-photometric determination of the elements[218-222]. Other polyfluoro-β-diketones are more rarely used in the extraction and spectrophotometric determination of metal ions[223-225], although perfluoroalkylvinylphenylpropanediones have been patented as monomers for the synthesis of polymers capable of extracting metals ions from highly acid media[226], while β-diketones containing the pentafluorophenyl substituent together with a perfluoroalkyl substituent have been patented as extractants of vanadium from highly acid media[26,227].

2. The GLC Separation and Determination of Metal Cations

Fluorine-containing substituents increase the volatility of metal β-diketonates, which permits their gas-chromatographic separation and determination at much lower temperatures[228] and with the aid of electron-capture detectors; the sensitivity and selectivity of the analysis are thus improved[229]. The problems of the application of polyfluoro-β-diketones in the GLC of metal cations have been considered in a monograph[228] and the advances in recent years are described in reviews[229-234].

3. The Biological Activity of Fluorine-containing β-Diketones

Several forms of the biological activity of non-fluorinated β-diketones are known. The antiviral activity of α-substituted β-diketones and its relation to their structure[235-239], the antiallergic activity of α-cyano-derivatives[240], and the inhibition of the central nervous system by and the weakening effect of α-amino-β-dicarbonyl compounds on muscles[241] have been reported. A weak antitumour activity of β-diketones has been observed[242]. Derivatives of β-diketones have been patented as insecticides[243] and herbicides[244]. Few data are available on the biological activity of polyfluoro-β-diketones. The insecticidal activity of BTFA derivatives[245] as well as the fungicidal activity of TTFA and benzofuroyltrifluoroacetone[246] have been reported.

TFFA is also known to have an effect on enzymes. It has been shown that TTFA inhibits the oxidation of succinates[247, 248] and lowers the activity of cytochrome reductase[249-262] and malate dehydrogenase[263]. The mechanism of the action of TTFA on enzymes has not been elucidated, but it has been suggested that TTFA interacts with the components of the respiratory chain and not with the enzymes themselves, the inhibiting effect being attributed to the ability of TTFA to form complexes with iron[251]. The differences in the effects of TTFA on various enzymes are most probably associated with the differences in the structures of the membranes and not with the differences in the structures of the enzymes[262], the inhibition in plant mitochondria being weaker than in animal mitochondria[264]. As regards other β-diketones, it is only known that AA and BA prevent the thermal inactivation of enzymes[265] and that furoyltrifluoroacetone inhibits the electron transfer in the oxidation of hexacyanoferrate in mitochondria[266].

4. Other Applications

Apart from their wide-scale employment for the separation and determination of metal cations, polyfluoro-β-diketones have also other less familiar applications. It has been established, for example, that TTFA retards the corrosion of engine cylinders[267]; HFAA has been recommended as an additive preventing gel formation in polymer solutions for spinning[268].

A number of fluorine-containing β-diketones have been patented as compounds imparting water repellant properties to paper[35]. 4,4,4-Trifluoro-1-(2-naphthyl)butane-1,3-dione has been patented as an additive increasing the light sensitivity of mixtures polymerisable by light[269], and TTFA is used in the membranes of ion-specific electrodes, particularly for Ca^{2+} ions[270,271], and for impregnating electrode membranes designed for the determination of 'onium ions[272].

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Analysis of the present state of research into the chemistry, properties, and applications of fluorine-containing β-diketones permits the conclusion that, while the methods of their synthesis have been thoroughly developed and a number of their properties of applied and theoretical importance are known, many questions have still been little investigated. The study of the interaction of fluorine-containing β-diketones with eletrophiles (alkylation, acylation, reactions with fluoro-olefins, oxirans, and thi-irans), the expansion of studies on nucleophilic reactions, determination of quantitative data concerning the influence of the introduction of fluorine atoms on the properties and reactivity of β-diketones, as well as the study of reaction mechanisms are of interest. Studies and comparative estimates of the biological activity of fluorine-containing β-diketones and heterocycles based on them are promising.

During the preparation of the manuscript for the press, the synthesis of pentafluorobenzoylacetone (I, $R_F = C_6H_5$, $R = CH_3$) by the condensation of pentafluoroacetophenone with its enolate anion was reported. In view of the splitting of the signal due to the vinyl proton by the *ortho*-fluorine atoms, the authors postulate the enolisation of the resulting compound at the carbonyl group linked to the non-fluorinated substituent[273]. The existence of the enols of symmetrical β-diketones in the *cis*-form with an asymmetric hydrogen bond has been confirmed by photoelectron spectroscopy and it has been established that the upper limit to the barrier in the interconversion of the C_S-forms via the C_{2v}-form is 6 kcal mol^{-1}.[274] The ionisation potentials and the electronic spectra of TFAA and HFAA have been calculated[275]. It has been established by ^1H, ^{19}F, and ^{13}C NMR that the interaction of asymmetric fluorine-containing β-diketones with alcohols results in the preferential formation of adducts via the carbonyl group linked to the fluorinated substituent[276]; this confirms the mechanism of the interaction of β-diketones with nucleophiles described above. Pyrazolo-β-diketones have been obtained for the first time from fluorine-containing bis-β-diketones[277] and their high catalytic activity in the formation of polyurethanes has been established. A number of studies published during this period have been devoted to the interaction of polyfluoro-β-dicarbonyl compounds with urea[278] and its derivatives[279-281] and also to their condensation with amino-compounds containing a mobile hydrogen atom in the α-position: aminopyrazolone[282], aminocyclohexane[283], aminopyrazole[284], and substituted aminodihydroindole[285]. 1,2,3,3,8-Pentamethyl-7-oxo-5-trifluoromethyl-2,3,7,8-tetrahydro-1*H*-pyrrolo[3,2-*d*]quinoline has been patented as a source of blue-green laser radiation[285]. The formation of a γ-trifluoromethylpyridone in the condensation of TFAA with malonodinitrile has been demonstrated[286]. The polarographic reduction of polyfluoro-β-diketones has been investigated[287]. Numerous studies have been devoted to the

applications of polyfluoro-β-diketones in the extraction of metal cations[288–292].

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Modern Theories of the Adsorption of Polymers on Solid Surfaces

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Studies concerned with the theoretical description and experimental assessment of the state of adsorbed macromolecules as well as the experimental estimation of the thickness of the adsorption layer are examined. The methodological approaches based on modern physical and physicochemical procedures for the investigation of the structure of the adsorption layers are discussed and the accumulated experimental data are analysed in detail. The role of the configurational state of macromolecules in the adsorption layer and of its structure in the establishment of the properties of polymeric compound materials is emphasised.
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I. INTRODUCTION

Despite the large number of studies carried out on the adsorption of polymers from solutions on solid surfaces, questions associated with the theoretical description of the process and the experimental determination of its fundamental features still remain at the centre of attention. This is because it has not been so far possible to bridge the gap between theoretical predictions and experimental results. This review deals with the present state of the problem of adsorption on the basis of the results of studies carried out predominantly during the last five years. Hitherto the only surveys of this field have been a monograph[1] and reviews specially devoted to adsorption from concentrated solutions[2,3].

II. THEORETICAL DESCRIPTION OF THE CONFIGURATIONAL STATE OF ADSORBED CHAIN MOLECULES

One of the central problems of the theory of adsorption is that of the conformations of the adsorbed chains. In a number of studies, examined in detail previously[1], ideas were developed according to which adsorption takes place in the form of sequences of segments ["trains"], linked to the surface, and loops extending into the solution. The lengths of the trains and loops have been calculated by methods of statistical thermodynamics on the basis of the existing theories of polymer solutions as a function of the principal parameters of the polymer chain. In most cases simplified models, which do not take into account the real behaviour of macromolecules in solutions, were used for the calculations. Therefore, despite the fairly complex mathematical procedures, the theoretical density distributions of the segments of the polymer chain obtained near the surface permitted only a qualitative description of this distribution.

1. The Lal-Stepto Theory

A significant improvement of the model of adsorbed sequences of segments and loops was achieved by the studies of Lal and Stepto[4-6]. In contrast to the previous theories, in order to attain a better agreement between the results of the calculation and the real behaviour of the adsorbed chain, they took into account the excluded volume for the chain interacting with the surface and also considered the influence of the nature of the solvent, manifested by its interaction with the segments of the polymer chain and sites on the adsorbent surface.

However, the study was confined to the case of an isolated chain. It was based on the model of a chain on a tetrahedral lattice, the lattice sites being occupied either by chain segments or solvent molecules. The chain conformations in the lattice were calculated by the Monte Carlo method, with successive generation of different conformations. Homogeneous Markov sequences were generated with probabilities of a single-step transition P_{ij} specified in a way such that the resulting set of conformations was characterised by a Boltzmann distribution within the limits of a fairly long sequence. The conformations generated differed in their energies and, when the condition $U \leq 0$ was valid for the energy change in the generation of a new conformation, this conformation was adopted with a probability of unity, while in the case $U > 0$ the new conformation was adopted with a probability $\exp(-U/kT)$ and was rejected with a probability $1-\exp(U/kT)$. If the new conformation was rejected, the previous ("current") conformation was recalculated. In this case one can write

$$P_{ij}=1 \text{ for } U_j \leqslant U_i;$$

$$P_{ij}=\exp(-U_j/kT)/\exp(-U_i/kT) \text{ for } U_j > U_i;$$

$$P_{ii}=1-P_{ij}.$$

The initial conformation was selected arbitrarily as any allowed conformation. As stated above, the conformation whose energy U' was smaller or equal to the energy of the preceding conformation U was included in the sequence of chain conformations on the lattice, i.e. a random number x between 0 and 1 was selected and compared with the quantity

$$r=\exp(-U'/kT)/\exp(-U/kT).$$

If $r \geq x$, then each new conformation was added to the sequence of conformations and a sequence of any length could thus be constructed.

In previous studies no account had been taken of internal rotation. In the model developed here it was assumed that the transition from one conformation to another takes place as a result of changes in the rotational positions, following one after another, of only a small number of consecutive linkages (in the given case four), subject to the condition that the remainder of the chain does not undergo any changes. The position of this transitional region in the molecule is assumed to be stochastic in nature. Four is the minimum number of linkages which can be used to generate all possible chain configurations on a tetrahedral lattice.

In a calculation made by the Monte Carlo method account was taken of only those conformations in which the macromolecule interacted with the surface. The chain is then described by three energy parameters characterising the transition from the *trans*- to the *gauche*-conformations with an energy difference $\Delta\varepsilon_g$ (the *gauche*-conformation is known to have a higher energy). In the lattice account is taken of the energies corresponding to the following angles between groups of three or four bonds: 0°, +120°, and −120°.

We believe that the main disadvantage of the model[4] is the initial postulate in the calculations of the conformations of the adsorbed chain consisting in the assumption that one end of the chain is permanently fixed in the plane of the absorbent ("anchor" units). This postulate appears relatively unjustified and is not introduced by the same workers in other instances[6]. The normal excluded volume conditions for the lattice chain, namely the exclusion of multiple occupations of a single site in the lattice, were automatically included in the program for calculations of the conformations[6]. In addition account was taken of the interaction between segments at the nearest neighbouring sites with the aid of the parameter of the Flory theory:

$$\Delta\varepsilon_{12} = \varepsilon_{12} - \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22}).$$

In the model proposed the solvent molecule and the segment occupying adjacent sites have an energy ε_{12}, the solvent molecules in the lattice have an energy ε_{11}, and the adjacent segments have an energy ε_{22}. Thus, when the configuration changes, the segment passes to a site adjoining another segment, two segment–solvent contacts are broken, and solvent–solvent and segment–segment contacts are formed, the overall energy change being $-2\Delta\varepsilon_{12}$. For a chain on a tetrahedral lattice, the number of possible non-bonded nearest neighbours in relation to a given chain segment is two. Hence, for an infinite chain and a random distribution on the lattice of both segments and solvent molecules, the quantity $2\Delta\varepsilon_{12}/kT$ can be set equal to χ (the usual Flory–Huggins interaction parameter). It is assumed that adsorption also takes place for negative adsorption energies:

$$\Delta\varepsilon_s = \varepsilon_{2s} - \varepsilon_{1s}.$$

The calculations were performed for $\Delta\varepsilon_g = 0$, and $\Delta\varepsilon_{12} = 0$, i.e. for a chain with free rotation and adsorption from an athermal solution. For numerical calculations, use was made of segment–surface energies of $-0.5kT$ and $-0.9kT$ and of numbers of chain segments $n+1 = 31$, 51, 76, and 101 (which correspond to 30, 50, 75, and 100 bonds). The calculations made it possible to determine the average fraction of the adsorbed segments $\langle\nu\rangle$ as a function of the adsorption energy $\Delta\varepsilon_s/kT$ for a chain of 100 segments[4] and also the average maximum thickness of the layer $\langle\tau_m\rangle$. The quantity $\langle\tau_m\rangle$ is expressed in units of the distance between two planes in the lattice, which is $\sqrt{2}l/\sqrt{3}$, where l is the "skeletal" bond length.

A general tendency in the variation of conformations in the adsorption layer is that the fraction of bound segments increases and the thickness of the layer diminishes with increase in the energy of the bond between the segment and the surface[6]. The changes in $\langle\nu\rangle$ and $\langle\tau_m\rangle$ following a change in chain length are more pronounced for weak adsorption; $\langle\nu\rangle$ and $\langle\tau_m\rangle$ are less sensitive to chain length than the adsorption energy. It follows from calculations that, when $\Delta\varepsilon_s/kT = -0.9$, the adsorbed molecule is tightly fitted on the surface and the slight increase of $\langle\nu\rangle$ and decrease of $\langle\tau_m\rangle$ with chain length indicate an increased compatibility between the chain and the surface with increase in chain length.

The use of the familiar scheme of adsorbed trains and loops, differing in the allowance for the presence of unbound tails, in order to describe the conformations of adsorbed macromolecules, makes it possible to estimate the changes (in units of the number of segments) in the average lengths of the trains $\langle L_{tr}\rangle$, loops $\langle L_l\rangle$, and tails $\langle L_e\rangle$ as functions of the energy of adsorption and to show that $\langle L_{tr}\rangle$ and $\langle L_l\rangle$ do not vary significantly with adsorption energy (the length of the trains increases, while the size of the loops diminishes as the adsorption energy increases).

The changes in $\langle L_e\rangle$ are more significant consequently, at least in the case of weak adsorption, the thickness of the adsorbed layer is determined by the length of the tails. For $\Delta\varepsilon_s/kT = -0.8$, $\langle L_e\rangle$ is twice as large as $\langle L_l\rangle$ for all chain lengths. For weak adsorption, the chain length is proportional to the length of the tail. Analysis of the size distribution of the trains and loops shows that it is very narrow, while that for tails it is very broad. The quantities $\langle L_{tr}\rangle$, $\langle L_l\rangle$, and $\langle L_e\rangle$ can be used to characterise the so-called average adsorbed chain. If these quantities are known, the number of trains and loops can be determined[6].

Suppose that m is the number of trains which can be found from the equation

$$m\langle L_{tr}\rangle + (m-1)\langle L_l\rangle + 2\langle L_e\rangle = n+1,$$

and the fraction of bound segments is

$$\nu' = m\langle L_{tr}\rangle/(n+1).$$

Thus the quantities m and ν determine, together with $\langle L_{tr}\rangle$, $\langle L_l\rangle$, and $\langle L_e\rangle$, the configurational characteristics of the average adsorbed chain. Such quantities have been calculated for different n and $\Delta\varepsilon_s/kT$.

The size and shape of the adsorbed chain can be treated also in terms of mean square dimensions of the molecule $\langle r^2\rangle$ and the radius of rotation $\langle s^2\rangle$. The ratio $\langle r^2\rangle/\langle s^2\rangle$ for the adsorbed chain and the chain with free rotation in solution depends on n. The quantities $\alpha_r^2 = \langle r^2\rangle/\langle r_0^2\rangle$, where $\langle r_0^2\rangle$ are the unperturbed dimensions in solution, have also been calculated. They indicate an appreciable extension of the chains on the surface.

The results of the calculations make it possible to describe also the density distribution of the segments with respect to the thickness of the layer for different adsorption energies. For $\Delta\varepsilon_s = 0.5kT$, the density of the segments changes little in the first layers near the surface and then slowly decreases. For strong interactions, the initial sharp fall of the density is followed by a very much slower decrease. For adsorption from a non-athermal solvent, the model of an anchored chain has been adopted and $\Delta\varepsilon_g = 1.0kT$ and $\Delta\varepsilon_s = -0.5kT$.[4] The calculations were performed for a chain consisting of 100 segments.

The quantities $\langle r^2 \rangle$, $\langle s^2 \rangle$, $\langle \nu \rangle$, and $\langle \tau \rangle$ were calculated (see Table). The calculation showed that, for good solvents ($\Delta\varepsilon_{12}/kT = 0.50$ and 0.00), the molecules exist on the surface in the extended state. In a bad solvent the chain conformation is close to that of a coil[5]. Calculation[4] showed that the average fraction of adsorbed segments increases as the solvent becomes less effective and the thickness of the layer diminishes.

Calculated values of $\langle r^2 \rangle$, $\langle s^2 \rangle$, $\langle \nu \rangle$, and $\langle \tau \rangle$.

Curve	$\langle r^2 \rangle$	$\langle s^2 \rangle$	$\langle \nu \rangle$	$\langle \tau \rangle$
		a		
1	7327	709	33	19
2	5771	606	35	20
3	4307	493	39	18
4	2755	295	19	21
5	5355	682	34	27
		b		
1	1859	170	28	14
2	2267	172	44	9
3	2147	155	42	10
4	3011	247	34	14
5	1867	222	42	8
		c		
1	299	106	31	8
2	563	98	41	6
3	203	89	45	7
4	83	86	30	6
5	123	73	36	6

On the assumption of the "anchored" model, the conformations of the adsorbed chains are illustrated schematically in Fig. 1,[4] and the density distribution of the segments is shown in Fig. 2.[4] The conformation is shown as the height of each segment above the surface in a non-dimensional representation. Fig. 1 shows that, in a good solvent ($\Delta\varepsilon_{12} = 0.5kT$), there is a distinct tendency towards the formation of long trains in the initial part of the chain and there is an appreciable fraction of non-adsorbed segments in the tails.

The formation of loops is less favoured and only a few configurations contain more than two loops. The configuration consists very often of a bound train and a tail.

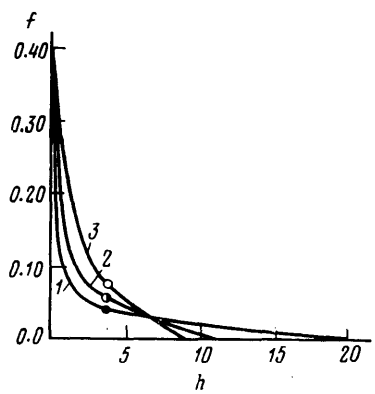


Figure 1. The calculated average fractions of bound segments in each successive layer over the plane of the adsorbent for different values of $\Delta\varepsilon_1$ (Clark et al.[4]); *1*) $0.5kT$; *2*) $0.0kT$; *3*) $-0.5kT$.

In a good solvent the repulsion of the segments leads to an extended rigid state of the chain together with a positive value of the parameter $\Delta\varepsilon_g$. This state induces a cooperative effect among the segments, leading to the formation of trains adjoining the anchored sections. This effect also leads to the appearance of groups of non-adsorbed segments behind the adsorbed train. Long trains and tails in a system with $\Delta\varepsilon_{12}/kT = 0.5$ can be regarded as the manifestation of the cooperative effect. The absence of loops can be attributed to the high energy required to bend the molecules.

In a bad solvent the probability of a strong interaction of the segments with one another and with the surface is a maximum. Therefore in the given case the molecules are in a tightly coiled state with a large number of segments bound to the surface. The presence of a relatively large number of loops is inevitable under these conditions.

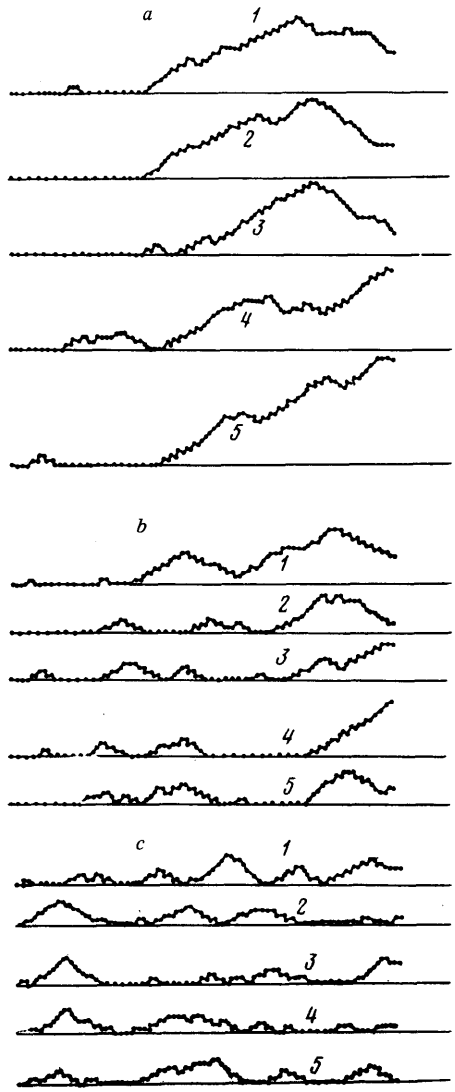


Figure 2. Certain typical configurations appearing with high frequencies in calculations by the Monte Carlo method[4]; $\Delta\varepsilon_1$: *a*) $0.5kT$; *b*) 0.0; *c*) $-0.5kT$; for the parameters of the curves, see Table.

The ideas of Lal and Stepto were described here in fair detail, since they must be regarded as a significant step forward in the theoretical description of adsorption, despite the fact that the model was developed for an isolated chain. On the basis of calculations of the conformations on a computer, the authors produced a cine-film demonstrating the behaviour of macromolecules near the interface and on the surface. This film was shown by Stepto at the IUPAC Microsymposium on Interfacial Phenomena in Prague in 1976. The film characterises the conformations of molecules in dynamic adsorption and desorption equilibrium and shows that in weak adsorption the molecules frequently leave the surface and assume the conformation typical for the molecules in solution. For strong adsorption, the molecule is retained closer to the surface and assumes an extended conformation. The author of this review was present at the showing of this film and can testify that the clarity of the representation makes it possible to illustrate the real picture of adsorption. A cartoon film characterising the behaviour of macromolecules in adsorption has also been made by Lumb[7].

2. The Hoeve Theory

Another fundamental approach to the theoretical estimation of the density distribution of segments in the adsorption layer as a function of the distance from the adsorbent surface is that developed by Hoeve[8-11]. The calculations were made for a single adsorbed chain consisting of n segments on the assumption that the loops are fairly large, but Hoeve did not take into account the effect of the excluded volume.

The number of segments at a distance from the surface in the range between z and $z+dz$ is defined as $n\rho(z)dz$, where $\rho(z)dz$ is the normalised function of the density distribution of the segments. The calculation performed for a one-dimensional lattice model yields[8]

$$\rho(z) = 4\pi^{1/4}\beta_1 C \exp[-4\beta_1 z(-\lambda)^{1/4}](1 + S_{-1/4} + S_{-3/4})^{-1}, \qquad (1)$$

where β_1 is determined by the condition

$$\beta_1^2 = 2\langle r_n^2\rangle_0/3n,$$

where $\langle r_n^2\rangle$ is the mean square distance between the ends of the free chain in the absence of volume effects, C a constant characterising the rigidity of the chain, λ the Lagrange multiplier, and $S_{1/2}$ and $S_{3/2}$ are functions of λ and of the size of the loops i.

Eqn.(1) is valid for $r > \delta$, where δ is the effective thickness of the segments adsorbed on the surface. It is seen that $\rho(z)$ is an exponential function of z for large loops and weak adsorption. For strong adsorption, the average size of the loops is small and the latter are not Gaussian chains. In this case the distribution depends on specific interactions, which are different for different chains. It is significant that in the chosen model there is a sharp decrease in the density distribution at distances from the surface exceeding the effective thickness of the segment $z = \delta$. In the adsorption layer near the surface ($0 < z < \delta$) Eqn.(1) is inapplicable; the fraction of bound segments is given by another relation and the density $\rho_a = P\delta^{-1}$, where

$$P = (1 + S_{-3/4})(1 + S_{-1/4} + S_{-3/4})^{-1}.$$

The density of the segments in solution at a distance $z = \delta$ is given by the equation

$$\rho(\delta) = K(1 + S_{-1/4} + S_{-3/4})^{-1},$$

where K is a numerical coefficient. Comparison of this equation with Eqn.(1) shows that the density falls for $z = \delta$.

For a real chain, more rigid than that assumed in the calculations, the decrease of density will be greater the more rigid the chain. This decrease is consistent with expectation, since there must be a compromise between the random distribution of the segments in all the layers and the greatest possible saturation of the first layer, where attraction takes place.

Hoeve[8] also calculated conformations taking into account the rigidity of the polymer chain. The rigidity parameter was introduced into the calculation of the number of random movements of the chain in a three-dimensional lattice in the form of a factor w when the step taken in the lattice was in the same direction as the previous one; if the step was taken in any of the four directions perpendicular to the previous one, the factor was unity.

The factor $w = \exp(-\varepsilon/kT)$, where ε is the difference between the energies of conformations in one of which two consecutive bonds lie in the same direction while in the other they are perpendicular to one another. If ε/kT diminishes, then w and hence the rigidity of the chain increase. In the limit, where ε/kT tends to an infinitely large negative value, the chain becomes rigid and rodlike. In the case where the first step in the lattice begins at the interface the partition function for a single chain is defined. The grand partition function for a chain fixed at one end at the interface is

$$\theta(s) = |E|^{-1}\{\{(\lambda - sw)^{-1} + s(1 - sw\lambda)^{-1}\}4s^2t +$$
$$+ \{s + s^2(\lambda - sw)^{-1} + s(1 - sw\lambda)^{-1}\}\{1 + (2 - w)st\}(1 - \lambda)^{-1}\};$$

where $s = \exp\mu/kT$, $|E|$ is a function of w, s, t and λ, and μ is the chemical potential of a monomer unit under the conditions of the equilibrium distribution of the N-mers bound to the surface by one end only; $t = \exp(-\varepsilon_a/kT)$, where ε_a is the adsorption energy (the necessary condition for adsorption is $\varepsilon_a < 0$ and $t > 1$) and λ is the Lagrange multiplier. The average number of bonds in the chain can be found from the equation:

$$\langle N\rangle = \partial \ln\theta/\partial \ln s$$

while the average number of bonds adsorbed at the interface is $\langle N_0\rangle = \partial \ln\theta/\partial \ln t$. Then at a distance from the surface the average number of segments in the layer is $\langle N_0^k\rangle = [\partial \ln\theta/\partial \ln u]$, where u is the exponent of the polynomial in the function describing θ. Calculations showed that, for low values of λ, the density of the segments decreases sharply on moving away from the surface and that the majority of the segments are adsorbed in the first layer. Only when λ approaches 1 does the density of the segments near the surface become appreciable. In the limit at $\lambda = 1$ the density of the segments near the interface is a maximum and constant for all the layers. The critical values of t for adsorption are in this case defined by the relation

$$t = (w+4)^2(w^2+6w+12)^{-1}.$$

Thus, whereas previously Hoeve[8] introduced the flexibility parameter C for the Gaussian chain, which is difficult to determine quantitatively, in the present model the flexibility of the chain is taken into account by the parameter w, which constitutes an advantage of the approach under consideration. For an adsorbed chain consisting of a sequence of adsorbed segments and loops, the following relation holds:

$$\theta = \theta_{tr} + \theta_{loop} = 1,$$

where θ is the grand partition function, which is a function of the ratio of the activities of the adsorbed and free chains and θ_{tr} and θ_{loop} are the grand partition functions for trains and loops. It can be shown that

$$\theta_{tr} = (w+2)st[1-(w+2)st]^{-1},$$
$$\theta_{loop} = 4s(\lambda - sw)\ (1-sw\lambda)^{-1}(w+2)^{-1}.$$

At the same time Hoeve[9] emphasises the unrealistic nature of the model which he chose, as well as all other models examined previously. However, he reaches the important conclusion that the sharp subdivision into surface and diffuse layers is artificial. In practice density as a function of distance depends on specific chain conformations. Unfortunately, the thickness of the layer cannot be determined exactly experimentally regardless of theoretical postulates. A specific density profile is usually postulated beforehand after which the average thickness of the layer is calculated.

Hoeve notes that in such calculations one cannot ignore the effect of the excluded volume, which is bound to occur in real systems as a result of the interchain interaction. However, one can assume that, in the diffuse layer beyond the interface[10,11], the effects of the excluded volume are insignificant if the volume fraction of the segments is much lower than at the interface.

3. Other Theories

The distribution functions examined above contain parameters which are virtually impossible to estimate for real systems. Despite this, the segment distribution functions have been modelled in a number of studies. Hoffman and Forsman[12] attempted to estimate the parameters of the distribution function on the basis of the Flory–Huggins theory of polymer solutions, but they began with the inadequately justified hypothesis that the adsorbed segments have the normal density. They analysed the Gaussian distribution and the distribution proposed by Hoeve[8] and proposed a double Gaussian model of the type

$$\rho = \rho_0[\exp\{-B^2(x^2+y^2)/\alpha_{xy}\}] \times [A\exp\{-z^2/B\} + (1-A)\exp\{-z^2/C^2\}],$$

where ρ is the density of the segments, α_{xy} the broadening factor for chains in the x and y directions, z the distance from the surface, x and y the distances along the surface, and A, B, and C are independent model parameters. In the z direction, perpendicular to the surface, the model can be reduced to the Gaussian distribution for $A = 0$ and is close to the Hoeve distribution for $B > C$.

A probability density distribution function has also been proposed[12] for the radius of inertia and has been used to represent the configurational entropy as a component of the free energy of the adsorbed molecules. A numerical algorithm has been proposed for the determination of the parameters of the distribution function by minimising the free energy at the interface. However, the calculations are very difficult and require a very large amount of computation.

A statistical method for finding the density distribution of the segments for an anchored chain has been proposed[13]. For a layer of constant density, the parameters of the distribution function have been determined from the equilibrium degrees of adsorption and the area of the monomer unit[14]. A distribution function taking into account the formation of surface layers of different thickness and the deformation of macromolecules in adsorption has been proposed[14] and used to estimate the average thicknesses of the layer. The results indicate a satisfactory description of the conformations of the macromolecules in the surface layer by the proposed distribution function and the possibility of its employment for the determination of the thickness of the adsorption layer.

Lax[15] examined the configurational behaviour of an isolated polymer molecule and the influence on the latter of the interaction with the solvent. The necessity for taking this into account was pointed out in an earlier study by Silberberg[16], who demonstrated theoretically that the influence of the solvent and concentration can induce appreciable conformational changes. Lax calculated the conformations by generating random self-avoiding movements in the lattice in the presence of an interacting rigid barrier. Relations were obtained for the mean square distance between the ends of the chain $\langle R_N^2 \rangle$ corresponding to different numbers of segments N and different adsorption energies and for the average and mean square distances from the end of the chain to the surface $\langle z_N \rangle$. Calculations showed that the latter quantities, determined taking into account the influence of the interaction with the solvent, are large. The average maximum quantity $\langle z_N^{max} \rangle$ increases with decrease in adsorption energy. The average numbers of segments on the surface have also been calculated as functions of the adsorption energy and the attainment of saturation for high energies ($\varepsilon > 2.2\ kT$) has been demonstrated.

The influence of the excluded volume of the conformations of the adsorbed polymers has also been examined in a study[17] where it was assumed that the density of the adsorbed molecules is high and homogeneous and that partial overlap of the molecules and their interaction take place on the surface. An expression was found for the critical value of the free energy of the adsorbed segments:

$$\varphi_c = \varphi_c^0(1 + 6n\nu z_0/l^2 + \ldots),$$

where ϕ_c^0 is the critical free energy of the adsorption of the segment at the θ-point, n the total number of adsorbed segments, l the bond length, z_0 the range of action of the adsorption potential, and ν the excluded volume defined by

$$v = (1/2 - \chi/V_2^2)V_1$$

(χ is the interaction parameter and V_2 and V_1 are the volumes of the segment and the solvent molecule).

The average thickness of the adsorption layer is

$$t(\gg z_0) = t_0(1 + 6n\nu t_0)/l^2,$$

where t_0 is the average thickness of the layer at the θ-point.

In recent years Hesselink developed a model of the structure of the adsorption layer[18,19], according to which the adsorption layer consists of a dense first layer, at whose boundary there is an abrupt change in the density of the segments, and of a loose layer of tails and loops directed towards the bulk of the solution. Hesselink[19] determined for a cubic lattice the distribution of the units in a macromolecule adsorbed by its end in a tail of i segments and in a loop (adsorption via two terminal groups) using a method similar to that developed by Hoeve[14].

The following function has been obtained for the distribution of segments in a molecule attached via the tail[19]:

$$\rho_1(x) = 6\,(il_c^2)^{-1} \int_x^{2x} \exp\{-3t^2/2il_c^2\}\,\mathrm{d}t,$$

where x is the distance from the surface, i the number of segments in the macromolecule, and l_c the length of the segment. The distribution of the segments in the loop is

$$\rho_2(x) = 12\,(il_c^2)^{-1} \exp\{6x^2/il_c^2\}\,.$$

From these equations, it is possible to find the mean square distance between the segments and the surface. For a chain attached at one end, $\langle x^2\rangle = \frac{7}{18} il_c^2$, and for a chain attached at two ends, $\langle x^2\rangle = \frac{1}{6} il_c^2$. This calculation shows that the loop is more tightly compressed on the surface than the tail comprising the same number of segments only by a factor of $\sqrt{7/3}$. This distribution can be applied also to a chain adsorbed by several loops, provided that the number of segments in each loop is the same. This problem was examined in detail by Hesselink[19], who analysed statistically the changes in the configurational properties of adsorbed macromolecules as an impermeable surface is approached.

The distribution functions have also been calculated for the adsorption of the molecules of copolymers in which the size distribution of the loops is determined by the distribution of the lengths of sequences of different units. The distribution curve for the case of a large number of loops is less steep than for the distribution in the case of only one loop. It is significant that in the adsorption of a copolymer via one loop the density in the immediate vicinity of the surface is lower than at some distance from the latter. This is because in a homopolymer any segment can be sorbed, while in a copolymer only a segment capable of interaction can be sorbed[19].

Next Hesselink examined the configurational free energy of the tails, loops, and bridges formed by macromolecules between particles (in connection with the consideration of the problem of the stabilisation of colloid particles and the behaviour of macromolecules between two adsorbing planes). The case of the mutual approach of particles coated by adsorbed molecules, where the adsorption layers should be capable of interpenetration, was examined; the density distribution of the segments in the tails and loops then changes as the two surfaces approach one another[20].

It has been suggested[21,22] that the density of the segments decreases with the distance from the surface and that the effective density of the adsorption layer is related to the average size of the loops in the same way as the change in the density of the segments $\rho(\tau)$ of a free coil with the distance from its centre of gravity is related to the number of segments in the macromolecule, i.e. it is assumed that $\rho(\tau) = \rho_{\text{eff}}$ for $\tau = \Delta$ (Δ is the thickness of the layer). This is a fairly rough approximation, since the density distribution of the segments in solution is Gaussian and that in the adsorption layer is in most cases exponential.

Theoretical calculations of the density distribution of the segments and of the thickness of the layers are important for the description of processes involving the stabilisation of dispersed particles by polymers or their flocculation. These problems, associated with the structure of the adsorption layer, have been discussed in detail in a number of studies[20,23,25]. They are based on the postulate of the adsorption interaction of the macromolecules with two flat plates.

Using a simple model of the macromolecules adsorbed on two parallel plates with a specific surface area A and separated by a distance L, it is possible to calculate the resultant pressure on the plates under conditions of repulsion associated with configurational entropy[24]. Neglecting the adsorption of the polymer on the surface, the conformations of a chain with a specified length N, beginning at a point r on the surface and terminating at a point r' in the gap between the plates, are then calculated by statistical methods. The free energies can then be found from the expression for the partition function for such a chain and can be used to obtain the effective pressures. For plates remote from one another ("short" polymer chains) and for plates close to one another (long chains), the following equations have been found (l is the chain length):

$$p = -\frac{1}{A}\frac{\partial F}{\partial L} = \frac{kT}{AL}\left[1 + \frac{2}{\pi^{1/4}}\left(2\,\frac{Nl}{3L^2}\right)^{1/4}\right],$$

for the case where $2Nl/3L^2 \ll 1$ and

$$p = \frac{kT}{AL}\left[\frac{4\pi\rho^2 N}{3L^3} + 1 \ldots\right].$$

for $2Nl/3L^2 \gg 1$.

These theoretical results show that the polymer adsorbed on the surface can stabilise colloid particles by virtue of the repulsion due to the entropy factor. On the other hand, flocculation can occur in the case of strong adsorption of polymer segments on the surface of the colloid particles.

4. The Adsorption Isotherm of Compact Macromolecules

In the studies discussed above the problem of adsorption isotherms, which had been the subject of thorough investigations in previous years[1], was not considered. A new feature in this field is Silberberg's attempt[26] to derive an equation for the adsorption of compact macromolecules, which include those of biopolymers present in solution in the form of dense self-aggregated globules. It is assumed that the electrostatic effects specific to given systems are of secondary importance compared with the large size of the macromolecules (for a high ionic strength of the solution and a sufficient charge separation in the molecules) and one considers a compact ("cubic") macromolecule whose volume is greater by a factor P than that of the solvent molecule. In a three-dimensional lattice such a macromolecule occupies P sites. If each site in the lattice has c_B neighbours in the

bulk phase and c_S neighbours on the surface, then the macromolecule itself in its natural coiled conformation is characterised by the following number of interactions:

$$\frac{1}{2}Pc_B-(P-1)-\frac{1}{4}P_S(c_B-c_S),$$

where P_S is the number of segments on the surface of the compact molecule. In adsorption z out of the P_S outer segments are bound to the surface. Then, for a cubic molecule, the adsorption would extend from the surface into the bulk phase over $1/p=P/z$ layers, forming the surface phase, among which only the first layer is in direct contact with the surface, but all the $1/p$ layers have the *same* concentration of polymer segments (in contrast to the adsorption of the usual flexible chains)[26] (here p is the fraction of segments bound to the surface).

If there are M^S sites and N_p^S polymer molecules on the surface and N_0^S solvent molecules form the surface phase, then

$$(1/p)M^S=N_0^S+PN_p^S.$$

If the system contains N_p^T polymer molecules and N_0^T solvent molecules, then the bulk phase contains $N_p=N_p^T-N_p^S$ polymer molecules and

$$N_0=N_0^T-N_0^S=N_0^T-(1/p)M^S+PN_p^S$$

solvent molecules.

We shall define $\theta=xN_p^S/M^S$ and $\Phi^*=PN_p/(N_0+PN_p)$ as the degree of surface coverage and volume saturation. For specified M^S, N_p^T, and N_0^T, these quantities are a function of N_p^S alone. If the unmixed pure polymer phase comprising N_p^T molecules and the solvent phase comprising N_0^T molecules in contact with M^S sites are regarded as the initial state, it is possible to determine the number of different configurations on mixing in contact with the surface subject to the condition that all the configurations have the same energy. When there is a difference between the energies of the configurations, i.e. when the energies of the polymer–polymer, solvent–solvent, and polymer–solvent junctions are different, it is possible to determine the energy of mixing of the macromolecules with the solvent in the presence of a surface:

$$\Delta U/kT=\chi(c_pz/c_BP)(PN_p)N_0/(N_0+PN_p)+$$
$$+\chi\{(c_p-1)z/c_BP\}(PN_p)N_0^S/(N_0^S+PN_p^S)-\chi_S(z/c_{SB}P)(PN_p^S),$$

where χ is the usual Flory–Huggins parameter, χ_S a parameter characterising the sorption of a flexible molecule, and c_p the coordination number.

Starting with these postulates, one can find the partition function determined by the maximum in the derivative of $\Omega\exp(-\Delta U/kT)$ with respect to the single independent variable N_p^S:

$$\partial\ln[\Omega\exp(-\Delta U/kT)]/\partial\ln N_p^S=0.$$

Hence we obtain finally an expression for the adsorption isotherm:

$$\ln(\theta/\Phi^*)=P\{\ln(1-\theta)/(1-\Phi^*)+p\ln p+(1-p)\ln(1-p)+$$
$$+(p\chi/c_B)[c_p(1-2\Phi^*)-(c_p-1)(1-2\theta)]+p\chi_S/c_{SB}\}.$$

Comparison of the theoretical isotherms obtained by plotting the number of equivalent monolayers $\theta/p=P^{1/3}\theta$ against the volume fraction of the polymer in the solvent with the degree of adsorption of flexible chains shows that the degree of adsorption of compact chains is greater and the fraction of the polymer on the surface $p=P^{-1/3}$ and the degree of surface coverage θ are smaller than for flexible chains. Consequently the surface layer is less compact. Calculation also shows[26] that in this case the possibility of a change in conformation in the surface layer (the uncoiling of the chain) plays an insignificant role.

However, in real systems, in the case of the adsorption of charged and compact macromolecules, there is a possibility of other relations. It has been shown[27] that there is virtually no adsorption of poly(methacrylic acid) (PMAA) in the globular unionised form from aqueous solutions. However, the nature of the adsorption of ionised PMAA [28] is determined by the charge on the adsorbent surface (the ζ-potential of its particles). The surfaces of alumina and quartz are negatively charged and the degree of adsorption of negatively charged macromolecules diminishes. Thus electrostatic effects, which cannot be described by statistical theories of adsorption, can play a decisive role in the given case.

The complexity of the theoretical description of the adsorption interaction of polymers with the surface of a solid absorbent consists in the fact that in such systems a number of inter-related phenomena occur during the adsorption process. It has now been established that the degree and nature of adsorption depend significantly on the formation of aggregates of macromolecules and the development of coagulation in the disperse phase[2,3,20]. On the other hand, the adsorption of the polymer is responsible for the establishment of a new aggregate–macromolecule equilibrium and also alters the rate of coagulation of dispersions. As a consequence of such correlation, an unambiguous interpretation of the experimental data obtained is in many instances impossible.

For a theoretical determination of the mechanism of the adsorption interaction at the interface, it is necessary to consider also the kinetics of all the processes occurring in the adsorption of macromolecules in the dispersions, namely the adsorption and aggregation of macromolecules and the coagulation of the disperse phase. Such a treatment, carried out by Lipatov et al.[29], has been based on Smoluchowski's kinetic equations for the coagulation of dispersions[30]. If macromolecules and their aggregates are considered as separate kinetic units, analogous to colloidal particles, then the kinetics of the aggregation of macromolecules and the kinetics of adsorption can be described by analogous equations.

The system of differential equations thus obtained cannot be solved analytically but, with the aid of numerical methods, it is possible to obtain on a computer the overall time pattern of the changes in the number of macromolecules, the particles of the solid phase, and their aggregates, as well as adsorbed macromolecules as functions of the size distribution of the micro-objects. The size distribution functions of macromolecules, the particles of the disperse phase, and the adsorbed macromolecules, characterising

the establishment of an equilibrium between the macromolecules, the particles of the solid phase, and their aggregates as a function of time and making it possible to follow the transition from the initial to the final equilibrium, were thus obtained.

5. The Application of Computer Modelling Methods in the Calculation of the Conformations of Adsorbed Chains

Computer modelling methods have been widely used recently to estimate the conformations of adsorbed polymer chains[31-35]. The configurational properties of oligomers have been calculated by the total sorting method, based on the generation of all possible N-unit chains, with subsequent extrapolation to high polymers[33]. Computer modelling has been carried out for chains with $N \leq 14$ on a cubic lattice with four selections, the energy of the junction between a section of the chain and the surface being varied from 0 to $1.5kT$. The number of segments on the surface, the number of returns to the surface (the number of loops), the length of the normal from the end of the molecule to the surface and its square, the distance from the surface to the most remote segment, and the distance between the ends of the chain were determined. These computer simulations showed that, with increase of adsorption energy, the mean square distance between the ends initially diminishes to a minimum at $-\varepsilon/kT = 0.375$ and then increases. The curves relating the number of loops to $-\varepsilon/kT$ pass through a maximum at $-\varepsilon/kT = 0.75$.

Thus the extremum values of different properties of the polymer chain are observed for different energies of their interaction with the surface. The calculations demonstrated the validity of the empirical relations $\langle R_N^2 \rangle = \alpha N^{\gamma}$, where α and γ are constants. For $-\varepsilon/kT \cong 0.5$, the quantity γ is close to 1.30, while for high interaction energies γ increases until it reaches, at $-\varepsilon/kT = 0.875$, the value 1.47 characteristic of two-dimensional lattices (1.50). This finding demonstrates the virtually complete adsorption of the polymer on the surface for $-\varepsilon/kT \geq 0.875$. It has been shown that, for energies $-\varepsilon/kT \geq 0.75$, the average distance between the most remote atom of the chain and the surface is less than two lengths of the chain.

The mean squares of the distance between the ends of the chains $\langle R_N^2 \rangle$ and of the radius of inertia $\langle s_N^2 \rangle$ as well as the average number of closed chains (not only beginning but also terminating on the surface) have also been estimated[32]. The conformational characteristics have been calculated for $N \leq 14$ and for different values of $-\varepsilon/kT$. It has been shown that, for open chains at $-\varepsilon/kT \to 0$, surface effects do not play any role, the ratio $\langle s_N^2 \rangle / \langle R_N^2 \rangle = 0.1314$, and the power exponent $\gamma = 1.20$. With increase of $-\varepsilon/kT$, these quantities change somewhat and the ratio $\langle s_N^2 \rangle / \langle R_N^2 \rangle$ diminishes sharply only for $-\varepsilon/kT \geq 1.6$ (critical value). The oligomer chain is then virtually completely sorbed on the surface. The behaviour of closed chains obeys another statistic. For such chains, $\langle s_N^2 \rangle / \langle R_N^2 \rangle \to 0.200$ and $N \to \infty$. It has been noted that the models considered in computer simulations are also useful for the derivation of information about the entropy effect associated with the folding of the chains in crystals, about the role of configurational effects in the stabilisation of colloidal solutions, etc.

The dependence on the molecular weight of the first and second moments of the extent of the chains attached to the surface at one end (by extent, we understand the maximum distance between the planes bounding the chain segments[34]) has also been calculated by the method of the total sorting of configurations. The calculations were performed for a tetrahedral lattice with prohibition of self-intersections of the chain and $N = 5-14$. It was shown that, if the average extent is represented by the expansion $\langle x_N \rangle = AN^{\gamma} + BN^{\gamma-1} + \ldots -1$, then the asymptotic value of γ for the adsorbed chains at $1/N \to 0$ is 0.53, which is somewhat smaller than the corresponding value for chains which do not interact with the surface (0.61). The mean square of the radius of inertia $\langle s_N^2 \rangle$ is proportional to a $N^{1.27}$ according to calculated data, i.e. the power exponent for adsorbed chains differs from the exponent characteristic of all non-intersecting three-dimensional chains (6/5). Apart from the average characteristics, different distribution functions have also been obtained[34]. It has been shown that they change sharply if, instead of the prohibition of self-intersections, one introduces the parameter of the interaction between chain segments. If this parameter is sufficiently large, certain distribution functions become bimodal or multimodal.

One should note that the average changes in the internal and free energies, the entropy, the heat capacity, and the effective coordination number have been calculated as a function of $-\varepsilon/kT$ by the total sorting method for non-intersecting chains at the boundary with the surface[35]. For certain values of $-\varepsilon/kT$ (1.8), the plots of C_V/k against $-\varepsilon/kT$ (C_V is the heat capacity at constant volume) pass through a maximum, which indicates a second-order phase transition. At the transition point the mean squares of the distance between the chain ends and of the radius of inertia reach a minimum. When the specific energy of the interaction of the chains with the surface is attained, the system becomes two-dimensional, which corresponds to the adsorption of the polymer on the surface.

The machine experimental methods in relation to problems of the adsorption of polymers were developed further by Birshtein and coworkers[36-39]. It was shown that increased rigidity of the chain facilitates the adsorption process and increases the fraction of adsorbed units. It follows from the results of [38,39] that, in the region of strong interactions with the sorbent, the chain "spreads out" on the surface via its extended sections. Calculation of the free energy of adsorption showed that, for the critical energy of adsorption, the polymer chain undergoes a second-order phase transition, which is consistent with Lax's results[35]. The computer simulation also made it possible to estimate the fraction of chain segments linked directly to the surface as a function of chain length and the adsorption energy[38]. The calculation of the structure of the chains in the surface layer[39] is also of interest.

III. EXPERIMENTAL ESTIMATION OF THE STRUCTURE OF THE ADSORPTION LAYER

Despite the different attempts to calculate the conformation of adsorbed chains near the interface, a direct comparison of the results of such calculations with experiment still does not yield satisfactory agreement. This is because in the majority of calculations simplifying assumptions, which do not hold in real systems, are made. For example, one always calculates the conformation of isolated chains, whereas all the experimental results reflect the existence of a large number of chains competing for surface sites. As a result, the conformations of real chains are very different from those calculated theoretically for isolated chains. From this standpoint, the experimental estimation of the conformations of adsorbed chains and of the thickness of the adsorption layer is still of significant interest.

1. The Hydrodynamic Thickness of the Adsorption Layer

Theoretical ideas concerning the hydrodynamic thickness of the adsorption layer, based on fundamental hydrodynamic equations, have been developed[40]. The calculations are based on the following experimental fact: the rate of flow of the polymer solution through a capillary diminishes as a result of the adsorption of the polymer on the walls. The measurement of this change makes it possible to calculate the hydrodynamic thickness of the adsorption layer, which is defined as follows:

$$L_H = R[1-(I_v/I_v^0)^{1/4}],$$

where I_v and I_v^0 are the volumes of the liquid which pass through the capillary in the presence and in the absence of the polymer for the same shear stresses and R is the radius of the capillary.

The ratio I_v/I_v^0 is a complex function of R, b (where b is the average distance between the given monomer unit and the wall of the capillary), and the shielding factor b/d, where $d=(\eta/fn_0)^{1/2}$, η is the viscosity of the liquid, n_0 the density of the segments in the first layer at the surface, and d the frictional force between the polymer molecules and the liquid. An exponential distribution of the density of the segments near the interface and the parameters introduced in Hoeve's theory were used for the theoretical calculations. Theoretical relations between L_H and R/b were plotted for a number of values of b/l, for different volume fractions of the polymer in the first layer, and for three different chain lengths.

Comparison of the theoretical calculations with experiment showed that L_H varies linearly with the intrinsic viscosity $[\eta]$ and that the experimental thickness of the layer is of the order of magnitude of the size of the coil in the polymeric solvent. This yields the conclusion that the dimensions of the polymer coils are not distorted in the adsorption process[40].

The behaviour of the adsorbed molecule in the layer in contact with the flowing solvent is significant for the determination of the hydrodynamic thickness relative to the thickness of the adsorption layer of the polymer. This problem has been considered theoretically[41] on the basis of the Rouse-Zimm model for a polymer chain attached to the surface by one end. The main result of the calculations of the dynamic behaviour of the chain was to show that, in the Brownian movement of the anchored chain, the energy scattering exceeds by a factor of two the corresponding value for a free molecule in solution. These effects are attributed to the influence of the surface on the number of accessible conformations of the macromolecule.

Methods are available for the determination of the thickness of the layer from the apparent increase in the effective volume of the dispersed particles carrying the adsorption layer, which is determined viscometrically using an equation of the Einstein type and from sedimentation data[42,43].

The thickness of the layer is calculated with the aid of the sedimentation coefficient, which can be expressed in terms of the thickness of the layer δ and its density ρ_z for a particle with a radius a and a density ρ_1 in a liquid having a density ρ_0 by the following equation:

$$s^0=[2a^2(\rho_1-\rho_0)+2(3\delta a^2+3a\delta^2+\delta^3)\times(\rho_2-\rho_0)]/9\eta_0(a+\delta),$$

where s^0 has been adjusted to the zero concentration of particles. It is then assumed that the adsorption layer is a rigid impermeable cell. The density of the layer is determined as follows:

$$\rho_z=0.997+2.39\cdot10^{-7}\cdot4\pi a^2\Gamma/[{}^4/_3\pi(a+\delta)^3-{}^4/_3\pi a^3],$$

where Γ is the degree of adsorption on the plateau of the isotherm. When account is taken of this, one obtains

$$s^0=[2a^2(\rho_1-\rho_2)+1.434a^2\Gamma\cdot10^{-6}]/9\eta_0(a+\delta),$$

which is in fact used for the calculations[42,43].

As a result of the sedimentation and flocculation of particles coated by the adsorption layer, the rate of sedimentation decreases and the sedimentation half-period and the sedimentation volume increase, which can, in principle, yield information about the thickness of the adsorption layer. Thus the adsorption of poly(vinyl alcohol) has been studied[43] in the form of fractions with different molecular weights on polystyrene. It was found that the degree of adsorption and the thickness of the adsorption layer δ, calculated from the sedimentation data, increase with increase of $\bar{M}_w^{1/2}$. The volume occupied by the macromolecule in the adsorbed state is approximately equal to the volume of the effective hydrodynamic sphere of the poly(vinyl alcohol) molecules in the solution. However, δ is smaller than the effective hydrodynamic diameter of the polymer coils in solution. The results were interpreted in terms of the possible deformation of the coils without the mutual interpenetration or compression of neighbouring adsorbed macromolecules.

2. Calorimetric Methods

The use of direct calorimetric measurements of the heats of adsorption of polymers and the establishment of relations between them and adsorption isotherms, which makes it possible to estimate the enthalpy of adsorption and the number of bound segments, constituted definite progress in the study of adsorption[42,44-46].

The integral heat of adsorption is determined by the relation

$$-\Delta H(\theta)=-n\Delta H_{P,A}+n\Delta H_{L,A}+n\Delta H_{P,L}+\Delta H_{P,P},$$

where n is the number of points on the surface coated by the polymer segments, $\Delta H_{P,A}$ the enthalpy of binding per mole of monomer units, $\Delta H_{L,A}$ the heat of wetting per mole of active points on the surface, $\Delta H_{P,L}$ the enthalpy of desolvation per mole of adsorbed monomer, and $\Delta H_{P,P}$ the energy of the interaction of the adsorbed polymer molecules. If the last term is neglected, then

$$-\Delta H(\theta)=-n(\Delta H_{P,A}-\Delta H_{L,P}-\Delta H_{L,A}),$$

i.e. the enthalpy of adsorption is proportional to the number of centres on the surface and to a constant enthalpy contribution (the expression in brackets).

The differential enthalpy of adsorption is

$$D_A=\frac{d\Delta H(\theta)}{dN}=\frac{dn}{dN}(\Delta H_{P,A}-\Delta H_{L,P}-\Delta H_{L,A}),$$

where $N = A/M_M$ is the number of adsorbed polymer molecules in monomer units, A is the amount of the adsorbed polymer in grammes, and M_M the molecular weight of the monomer unit; thus D_A is a measure of the fraction of segments bound to the surface[46]. The enthalpies of adsorption of poly(ethylene glycols) of different molecular weights on aerosil have been determined experimentally. A linear dependence of the enthalpy of adsorption on the extinction coefficient of the band associated with the hydrogen bonds between poly(ethylene glycol) and aerosil (3300 cm^{-1}) was also established. The energy of the binding of poly(ethylene glycol), amounting to 41.4 kJ per mole of SiOH, which corresponds to the energy of the hydrogen bonds, was found from the enthalpy taking into account the density of the SiOH groups on the surface (which is 2.74/100 A^2).

The heat of adsorption data show that, along the initial sections of the isotherms, approximately 50% of the segments are bound, in satisfactory agreement with the estimates of the fraction of bound segments by infrared spectroscopy, and $p = 0.2-0.5$ at saturation. Thus calorimetric measurements yield, in principle, the same conclusions concerning the conformations of the macromolecules in the boundary layers as the other methods used previously[1]. However, calorimetric measurements yield more information about the mechanism of the adsorption and the interaction. The enthalpy of the adsorption per segment estimated from calorimetric data depends on the competing effects of the polymer–adsorbent, polymer–solvent, and solvent–polymer interactions[42].

A strong interaction between the solvent and the surface leads to a lower enthalpy of adsorption per segment than in the case of a non-polar solvent. In order to obtain a definite enthalpy of adsorption in a polar solvent, it is necessary that the degree of binding of the macromolecule be greater than in a non-polar solvent, which leads to a more planar conformation of the adsorbed macromolecule and to a smaller thickness of the adsorption layer.

In principle, when one considers the adsorption of polydisperse polymers, one must also consider the influence on adsorption of the particular level of thermodynamic incompatibility of fractions having different molecular weights, which follows from the dependence of the Flory–Huggins interaction parameter for the fraction χ_{23} or the parameter X_{23} of the new Flory theory on the composition of the mixture of polymer homologues[47]. A partial incompatibility of fractions of different molecular weight leads to the formation of molecular aggregates, which can be adsorbed on the surface independently. This follows from direct adsorption measurements[48], demonstrating the adsorption of aggregates of different structure, for a fairly broad molecular weight distribution, from solutions in a thermodynamically poor solvent.

In this connection one should note that at one time a number of workers[1] estimated the so-called isosteric heats of adsorption. The present state of the problem shows that these estimates cannot be regarded as correct. A change of temperature entails a change in the conformation of the polymer chain and in the interaction of the macromolecules with one another and with the solvent. As a consequence of this, when the temperature is altered, the conditions governing the junction between the macromolecule and the surface are different and the number of bound segments and hence also the overall enthalpy of adsorption per macromolecule (or the number of bound units) are not the same. One should also take into account the different adsorbabilities of high- and low-molecular-weight fractions and in principle the different temperature variations of their solubilities. All this suggests that the required results can be obtained only by the direct experimental determination of the heats of adsorption, as was done for the first time by Killmann et al.[42]

3. Spectroscopic Methods

The structure of adsorption layers has been studied by infrared spectroscopy[49] for linear saturated aliphatic polyesters and polystyrene. When the adsorbent is aerosil, the polyester is bound by hydrogen bonds on adsorption, as expected, which makes it possible to estimate the fraction of bound segments readily by infrared spectroscopy. For polyesters, this fraction is $p = 0.80$, which indicates the formation of layers with a relatively small number of loops. On the other hand, polystyrene does not interact with more than 50% of the surface hydroxyls via its benzene rings. The experimental adsorption isotherms can be described by the equation of the Langmuir isotherm.

Continuation of studies of the adsorption layers of various polymers by ellipsometric methods by Killmann and coworkers[50,51] permitted the subsequent development of a method based on the construction of isotherms for the thickness of the layer, the polymer concentration in the surface layer, and the degree of adsorption as a function of the solution concentration as well as the same quantities at saturation as a function of the molecular weight of the polymer. The influence of the molecular weight and the polarity of the polymer or adsorbent on these characteristics was established and a conclusion was reached concerning the possible conformations of the macromolecules in the adsorbed layer, which corresponds to the features already described and in our view leads to only isolated refinements in relation to specific polymers.

Thus it has been established that the thickness of the adsorption layer is described by the Mark–Houwink relation $d = KM^{\alpha}$, where M is the molecular weight and K a constant. For adsorption in the form of isolated coils, $\alpha = 0.5$ and for molecules extended on the surface, $\alpha \to 0$. An increase of α from 0.15 for low coverages to 0.5 for high coverages confirms the hypothesis that the conformation of the adsorbed chain depends on the solution concentration (degree of surface coverage). The dependence of the mean square thickness of the layer at the maximum solution concentration investigated (5 mg ml^{-1}) on the square root of the molecular weight (straight line) confirms that in the region of high concentrations the molecules are adsorbed in the form of a θ-coil[50,51].

Methods for the estimation of the conformations of adsorbed chains, based on the use of electron paramagnetic resonance (EPR)[52,53] have been developed in recent years together with the infrared spectroscopic method for the determination of the fraction of segments adsorbed on the surface. For this purpose, one uses polymers with a spin label, which gives rise to three lines in the EPR spectrum; their form and width being determined by the rotational correlation time. For a polymer adsorbed at the solid–solution interface, providing the spin label is distributed at random along the chain and does not influence the adsorption process, the differences in the mobilities of the side groups of the chains are clearly manifested in the width of the spectral lines and in their positions. The segments adsorbed in the form of trains on the surface have shorter correlation times than the segments in loops.

The adsorption of the *N*-vinylpyrrolidinone–allylamine copolymer on aerosil has been studied by this method[53]. The label was introduced by the interaction of the polymer via its NH_2 groups with 4-isothiocyanato-2,2,6,6-tetramethylpiperidine oxide (one label for five polymer molecules).

The ratio of the number of segments in the loops to the ratio of the number of segments in the adsorbed trains can be estimated from the EPR data for the linear polymer subject to the assumption made above. However, one cannot then take into account segments with intermediate mobility, i.e. the segments in the loops but close to the surface. Since the complex spectrum can be resolved into two simple spectra, it is suggested that the number of such segments is small compared with the total number of segments. It has been established by this method[52,54] that the conformation of the polymer chain varies from relatively planar to a conformation characterised by the presence of loops with increase of surface coverage of the adsorbent. This follows from the dependence of the fraction of adsorbed segments p on the degree of surface coverage.

Thus the overall pattern revealed by the EPR method is consistent with that already described on the basis of the results of measurements by other methods. However, the following result is of interest. It has been shown that, when an additional portion of pure sorbent is added to the sorbent saturated by the adsorbed polymer, a significant increase of the degree of binding of the segments p, determined by NMR, is observed[53]. This demonstrates the formation of bridges between different sorbent particles bound to the macromolecule, which is important for understanding the mechanism of the interaction of the dispersed particles following the introduction of polymer molecules into the disperse system. The authors suggest[53] that this effect is associated with the fact that some of the segments present initially in the loop are converted into an adsorbed train of segments as a result of the adsorption of added particles on the unoccupied surface. The formation of a bridge implies that some of the molecules pass from an adsorption-saturated particle to an unsaturated particle, which can entail an increase of p.

The application of the EPR method in the study of the influence of the solvent on the conformation of the adsorbed molecule showed that an impairment of the "thermodynamic quality" of the solvent leads to an increase of the fraction of segments in the trains of segments bound to the surface, which conflicts with Hoeve's data[10] showing that the size of the loops increases with "impairment" of the solvent.

The conformations of adsorbed chains have been studied experimentally[54] by high-resolution NMR in adsorption of poly(methyl methacrylate) on silica gel. The method is based on the decrease in the molecular mobility of the adsorbed chains (segmental mobility). Its advantage over infrared spectroscopy is its applicability to the study of stereoregular polymers. Isotactic and syndiotactic polymethacrylates served as the objects of study. The complete disappearance of the signal associated with the segmental mobility, observed by the authors, shows that the polymer forms a large number of contacts with the surface and that the loops formed are relatively short and immobile. Isotactic poly(methyl methacrylate) is adsorbed preferentially relative to the syndiotactic polymer, as shown by data for the adsorption of their mixture.

The NMR method has also been used to determine the molecular mobility in adsorption layers of polystyrene and polycarbonate on aerosil; it is significant that the measurements were performed in the adsorption system itself without separating the adsorbent[55]. The experimental data obtained demonstrated the dependence of the mobility at a given solution concentration on the adsorbent content, which made it possible to regard the structure of the adsorption layers as one formed by adsorbed isolated loops and chain aggregates, in agreement with the concepts developed by the present author[2,3].

4. Colloidal-Chemical Methods

Interesting possibilities for the estimation of the thickness of adsorption layers of polymers arise from the measurement of the ζ-potential of colloidal particles coated by the adsorbed layer of polymer. However, this method can be applied only to adsorbent particles of colloidal dimensions. When it is used, one measures simultaneously the degree of adsorption of the high-molecular-weight substance and its influence on the electrokinetic potential of the particles[56-58]. It is assumed that the decrease of the ζ-potential with increasing degree of adsorption of the polymer is due to the displacement of the slip plane to the bulk of the solution as a result of the formation of the polymer layer on the surface and that the adsorption of the polymer does not entail a change in the distribution of charges in the diffuse ionic layer. In this case[59]

$$\tanh\left(\frac{ze\zeta}{4kT}\right) = \tanh\left(\frac{ze\psi_\delta}{4kT}\right)\exp\left[-\varkappa(\Delta-\delta)\right].$$

On the basis of this equation, it is possible to calculate for each measured electrokinetic potential the distance of the slip plane from the surface, which is assumed to be the thickness of the adsorption layer. In this equation e is the elementary charge, δ the thickness of the Stern layer, ψ_δ the potential at the boundary of the Stern layer for which one adopts[58] the ζ-potential at the initial (unprotected polymer) sol, and $\varkappa$ the Debye radius.

This method has been developed in detail for polymer-stabilised sols by Kocherga and Baran[60], who determined also the dependence of the thickness of the layers on the degree of adsorption of polymers. According to their data, the thickness of the adsorption layers increases monotonically with increasing degree of adsorption, reaching 100–200 Å, which is in good agreement with other data. The fact that the thickness of the layer depends in the first place on the degree of adsorption and not on the molecular weight of the polymer led to the conclusion that the average length of the adsorption loops also depends little on the molecular weight[60,61]. However, it must be emphasised that the determination of the thickness of the polymer layers on the surface of colloidal particles from electrophoretic measurements constitutes a fairly rough approximation.

At the same time comparison of the thickness of the layers[61] of poly(ethylene oxide) with the dimensions of the macromolecules in solution permits the conclusion that the polymer chains are appreciably deformed on adsorption. The experimental data obtained by this method suggest that the degree of deformation of the coils in the adsorption layer decreases with increasing rigidity of the macromolecular chains[25,60].

IV. CONCLUSION

The problem of the conformations of the macromolecules and of the structure of the adsorption layers is closely related to the elucidation of the mechanism of the adhesion of polymers to solids. However, in this case we are dealing with an adsorption interaction uncomplicated by the presence of a solvent in the system.

The problem of macromolecular conformations in adsorption layers in polymer compositions, i.e. in the absence of a solvent, is very important from the theoretical and practical points of view. Few experimental data have as yet been obtained on the thicknesses of the adsorption layers in the

absence of a solvent and on the conformations of macromolecules in such layers[62-66]. The single theoretical study by Silberberg[67] concerning adsorption in the absence of a solvent is of significant interest. The initial postulate was that adsorption leads to two main consequences—to an increase in the extent of the interfacial zone, where there is a transition from one homogeneous phase to another, and to an appreciable alteration of the conformation of the macromolecules in this region.

The theoretical models of the adsorption considered previously, the most general form of which is that developed by Silberberg, do not predict interfacial zones of considerable thickness. In the usual models of loops of different dimensions the distribution of segments is described by an exponentially decreasing function of the distance from the surface with a characteristic width proportional to the average length of loops. For chains with a large molecular weight, this model predicts that their size is independent of the molecular weight and the observed dependence of the thickness of the surface phase on the molecular weight cannot therefore be explained. For this reason, the model which is more realistic takes into account the influence of "tails" and postulating that the thickness of the layers is determined mainly by the "tails" [19,67] and not by the loops and that the number of segments in the loops is smaller than in the "tails" (this is consistent with the results of the studies by Lal and Stepto described above). The distribution of the segments in the tails should depend on the molecular weight.

Silberberg[67] considered theoretically the distribution of the segments in a pure polymer phase (in the absence of a solvent) in contact with the surface. The treatment is restricted to completely flexible chains whose arrangements correspond to identical energies and are equally probable. It is assumed that, at a distance h from the surface, the macromolecules are not subject to its influence, i.e. their conformations are unperturbed. The molecules in the layer with a thickness h adjoining the surface are then perturbed. By introducing the distribution functions for the density of the segments at different distances from the surface and the distribution functions of the centres of gravity of the macromolecules, the author obtained simple expressions for the number of macromolecules adsorbed by a unit surface ("perturbed") in the form

$$h/PV_0,$$

where P is the number of segments and V_0 the volume of the segment. Among this number, on average PV_0/A_0h segments of each chain are adsorbed on the surface, A_0 being the area per segment on the surface. The fraction of adsorbed segments is then

$$p = V_0^{1/3}/h.$$

Since h is comparable to the mean square radius of rotation at least as regards the order of magnitude, $h \cong V_0^{1/3}P^{1/2}$, it follows that

$$p \simeq 1/P^{1/2}.$$

On the basis of this estimate, Silberberg concluded that the width of the interfacial zone is proportional to the average radius of rotation and that in this region only a small section of the segments are in actual contact with the surface and that the "tails" exert the dominant influence on the thickness of this zone. According to Silberberg, the extent of the interfacial region is a consequence of the fact that the unperturbed macromolecules cannot approach the surface to a distance shorter than the radius of rotation and the remaining space is therefore filled with macromolecules with perturbed conformations. Because of this, the adsorbing surface exerts a significant influence on the form of the distribution functions of the segments and the centres of gravity of the macromolecules. This concept is closely related to the concept of the long-range influence of the surface on the structure of the adsorption layer, developed previously by the present author[1], and therefore confirms theoretically the numerous experimental facts that accumulated in earlier studies[1,68].

The above analysis of experimental data shows that, despite the definite progress achieved in recent years in the study of the structure of adsorption layers, and the development of fairly reliable methods for the estimation of their thickness, the problem of the conformations of the macromolecules at the interface remains open. The present author believes that this situation to some extent reflects that which has arisen in the study of molecular conformations in the amorphous state, where conflicting views exist[69-71]. At the same time it is evident that further investigation of this problem is of primary importance for the physical chemistry of polymeric compound materials.

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Study by ESR and Optical Spectroscopy of Transition-metal Ions in Zeolites and of Their Complexes with Adsorbed Molecules

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Studies by ESR and optical spectroscopy of zeolites containing transition-metal ions are reviewed. The locations of transition-element ions introduced into zeolites of various types by cation exchange and identified by these techniques are generalised. It is shown that these methods give useful information on the accessibility of the ions by adsorbed molecules and on the electronic structure of the complexes formed by the interaction betweeen adsorbed molecules and transition-metal ions. The properties of these complexes are discussed. 122 references.

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I. INTRODUCTION

Cation-exchange forms of zeolites are being used increasingly as catalysts, adsorbents, etc., and many papers on these materials have been published recently. ESR and optical (u.v.) spectroscopy methods have been used to identify the state of the cations in the zeolites, especially in the case of zeolites containing transition-metal ions. Very detailed information has been obtained by these methods: not only the valency and co-ordination states, and the localisation sites of the ions, but also the complexes formed by the interaction of the ions with various adsorbed molecules have been identified.

Mikheikin and coworkers[1] have reviewed the application of spectral methods of investigation to zeolites containing transition-metal ions, and the results obtained, but many new papers have appeared since that review was published. The more recent results have resolved the inconsistencies in some of the earlier work. A new review of the subject therefore seemed desirable.

The present review includes the whole of the work which has come to our notice since the publication of Mikheikin's review[1]. Most of the papers which we shall quote describe studies of ions from the first transition period (Ti–Cu), but we shall also discuss the more recent (and not very extensive) work on ions of metals from the second and third transition periods. With a few exceptions, dictated by the need for clarity in the discussion, we have avoided reference to work mentioned in Ref.1. The discussion is arranged in order of increasing atomic number of the transition elements incorporated in the zeolite, and the nomenclature used by Breck to denote the different localisation sites has been adopted[2].

II. IONS OF THE METALS FROM THE FIRST TRANSITION PERIOD

1. Titanium

The electronic configuration of the ground state of the atom is $(A)(3d)^2(4s)^2$, where (A) is the complete electronic structure of the argon atom. Titanium-containing type Y zeolites have been prepared and studied by ESR.[3] Ion exchange was carried out in an aqueous solution of $TiCl_3$, and it was assumed that after exchange the Ti^{3+} ions are located in the large zeolite holes[3].

Adsorption of oxygen and sulphur dioxide on these samples (after dehydration at 500 °C) produces ESR signals with the parameters $g_1 = 2.0196$, $g_2 = 2.0089$, $g_3 = 2.0031$, and $g_1 = 2.001$, $g_2 = 2.003$, $g_3 = 2.004$, assigned to the O_2^- and SO_2^- anion-radicals respectively. Adsorption of N_2O, followed by heating at 200 °C, gives an ESR signal with the parameters $g_1 = 2.017$ and $g_2 = 2.001$, tentatively assigned to the O^- anion-radicals. Since the adsorption centres are accessible to O_2, SO_2, and N_2O molecules they probably consist of Ti^{3+} ions localised in S_{II}, $S_{II'}$, or possibly S_{III} sites.

2. Vanadium

The electronic structure of the ground state of the atom is $(A)(3d)^3(4s)^2$. Vanadium has been introduced into zeolites only in the form of the vanadyl ion VO^{2+}. The localisation and mobility of vanadyl ions in type X and Y zeolites as a function of the degree of dehydration of the zeolite has been studied in detail by ESR at 77–300 K.[4]

Fully hydrated type Y zeolites at 20 °C give ESR spectra with the parameters $g_\parallel = 1.944$, $g_\perp = 1.978$, and $A_\parallel = 175 \times 10^{-4}$ cm^{-1}, $A_\perp = 70 \times 10^{-4}$ cm^{-1} (I), whereas at 77 K the spectral parameters are $g_\parallel = 1.938$, $g_\perp = 1.986$, $A_\parallel = 178 \times 10^{-4}$ cm^{-1}, $A_\perp = 70 \times 10^{-4}$ cm^{-1} (II). Reversibility of these spectral changes was demonstrated by dehydration at 350 °C followed by rehydration. In this case the dehydrated samples give an ESR signal with the parameters $g_\parallel = 1.917$, $g_\perp = 1.989$, $A_\parallel = 190 \times 10^{-4}$ cm^{-1}, $A_\perp = 79 \times 10^{-4}$ cm^{-1} (III), whose intensity increases with the dehydration temperature. Dehydration at temperatures above 350 °C gave irreversible changes in the intensity of the ESR signals, suggesting changes in the zeolite structure.

Both at −196 and at 20 °C the ESR spectra of fully hydrated type X zeolites gave a signal with the parameters $g_\parallel = 1.943$, $g_\perp = 1.983$, $A_\parallel = 170 \times 10^{-4}$ cm^{-1}, $A_\perp = 60 \times 10^{-4}$ cm^{-1} (IV), whereas after dehydration of the sample at 350 °C the parameters of the signal became $g_\perp = 1.989$, $g_\parallel = 1.918$, $A_\parallel = 178 \times 10^{-4}$ cm^{-1}, $A_\perp = 66 \times 10^{-4}$ cm^{-1} (V).

Spectra (I) and (IV) are similar to those of vanadyl ions in aqueous solution, and have been assigned[4] to VO^{2+} ions in large zeolite holes. Spectra (III) and (V) are believed to arise from VO^{2+} ions also localised in large holes but co-ordinated to OH^- or oxygen ions from the zeolite lattice. All these complexes have distorted octahedral surroundings with C_{4h} symmetry.

A study[5] of type Y zeolites containing vanadyl ions has shown that the VO^{2+} ions are stabilised mainly in S_{III} (and some S_{II}) sites by dehydration at temperatures up to 350 °C. Interactions between neighbouring vanadyl ions can be detected at exchange levels higher than 20%.

3. Chromium

The electronic configuration of the ground state of the atom is $(A)(3d)^5(4s)^1$. The commonest oxidation states of the chromium ions in solution under ordinary conditions are Cr^{3+} and Cr^{6+}. Because of the difficulty of introducing complexes with a charge greater than three into the zeolites all the work so far reported (with a few exceptions[6–8]) has been on zeolites prepared by exchange with trivalent chromium compounds.

Leaving aside the work on the localisation sites and on the properties of Cr^{3+} in zeolites, which has already been reviewed[1], we shall examine only the most recent work. The following zeolites have been studied[9,10] by ESR: CrNaA (8% exchange), CrNax (9.3% exchange), and CrNaY (13.6% exchange). The complex ions $Cr(H_2O)_6^{3+}$ and $Cr(NH_3)_6^{3+}$ were shown to be present, after exchange, in the S_{IA} and S_{II} sites of the type A and X zeolites and in the large holes of the type Y zeolites. We should note that in type A zeolites the symbol S_{IA} denotes the cation stabilisation sites in the hexagonal windows of oxygen ions giving access to the cubo-octahedra[2] whereas in type X and Y zeolites the same sites are denoted S_{II} or $S_{II'}$ (depending on the side of the window plane in which the cation is stabilised). Treatment of the zeolite in a stream of dry air at 350 °C causes oxidation of the Cr^{3+} ions to the Cr^{6+} and Cr^{5+} states, though the proportion of quinquevalent cations is always small. Between 80% (type A) and 30% (type X) of the originally present Cr^{3+} ions is oxidised. The parameters of the ESR spectra of the Cr^{5+} ion in oxidised chromium-containing A, X, and Y zeolites are consistent with the formation of chromyl ions (CrO^{3+}) in an octahedral configuration. The perpendicular component of the ESR spectra showed a hyperfine structure assigned[9,10] to the aluminium atoms of the zeolite skeleton. However, the proposed model includes four oxygen ions from the lattice as equatorial ligands, which it is difficult to reconcile with the suggestion that the cations are localised preferentially in S_{II} (or S_{IA}) sites to give a C_{3v} (or D_{3h}) symmetry. We should also note that the oxidation of chromium ions to Cr^{5+} and Cr^{6+} must involve some breakdown of the zeolite crystal lattice[1].

Vogt and coworkers[11,12] studied CrNaY zeolites with different chromium content by optical spectroscopy, and showed that on dehydration the chromium ions are localised initially in S_{II} sites (at 200 °C), then in $S_{I'}$ or $S_{II'}$ sites (400 °C) and lastly (at least partly) in S_I sites (500–600 °C). The occupation of S_I sites is inferred from the appearance of absorption bands at 14 300 and 18 800 cm^{-1}. This red shift from the spectrum of the hexa-aquo complexes (16 400 and 23 600 cm^{-1}) is explained by postulating that the lattice oxygen is a weaker ligand than the oxygen in a water molecule. Similar conclusions were obtained from X-ray diffraction studies.

Vacuum heat treatment at 450 °C suppressed the ESR signal from the Cr^{3+} hexa-aquo complex ions[11,12], indicating a transition from octahedral co-ordination of the chromium ions to a tetrahedral co-ordination distorted along a trigonal axis[1]. This conclusion was confirmed by measurements of magnetic susceptibility as a function of temperature. It was pointed out that heat treatment in a stream of dry air at 450 °C causes breakdown of the zeolites as a result of the oxidation of the Cr^{3+} ions to Cr^{5+} and Cr^{6+}. Breakdown is produced also by dehydration of the chromium-containing zeolites when the degree of exchange is more than 40%. Breakdown of the crystal structure of chromium-containing zeolites under oxidising conditions was first suggested in Ref. 13.

Thus the work published since the last review[1] is mainly a confirmation of previous results. The only novel feature is the discovery of Cr^{3+} ions in S_I positions in samples dehydrated at 500–600 °C.[9,10]

We shall now review the work on the adsorption of some molecules on chromium-containing zeolites. Formation of cation radicals has been observed during adsorption of naphthalene, anthracene, and perylene on CrNaY samples heat treated in a stream of air at 150–400 °C,[14] and ascribed to interactions of the Cr^{6+} ions with adsorbed molecules in the large zeolite holes. However, as we have already pointed out, the chromium-containing zeolites tend to break down under these conditions, and it is no longer legitimate to assume the presence of large holes.

The adsorption of nitric oxide and nitrogen dioxide on chromium containing type Y zeolite and mordenite is discussed in Ref.15. If the zeolites are oxidised at 500 °C the adsorption of NO and NO_2 produces ESR signals only from molecules loosely bound to the surface, whose characteristic ESR spectra are well known. However, if the same molecules are adsorbed on zeolites which have been reduced in hydrogen after the oxidising treatment a new ESR signal appears ($g_\perp = 2.000$, $g_\parallel = 1.917$ for both molecules and both types of zeolite): this is ascribed to the formation of complexes with the d^5 electronic structure (Cr^+NO^+ and $Cr^+NO_2^+$ for the NO and NO_2 molecules respectively). These complexes are formed by the interaction between the adsorbed molecules and the Cr^{2+} ions produced by the reducing treatment. We should once again point out that although the zeolites used in this work[15] had been reduced in hydrogen they had been previously subjected to an oxidising treatment, which must have destroyed the crystal structure and produced an amorphous alumina–silica. This probably explains why identical complexes were obtained with faujasite and mordenite.

Studies of zeolites containing Cr^{2+} ions introduced directly from solutions have also been reported[6–8]. Kellerman and coworkers[6] studied the adsorption of oxygen on Cr(II)NaA zeolite dehydrated at 300 °C, and concluded that the Cr^{2+} ions (stabilised mainly in S_{IA} sites) produce weak oxygen complexes at room temperature, with optical spectra characterised by absorption bands at 4000, 10 000, 14 200, 18 000, 20 600, and 26 200 cm^{-1}. Further work[7] showed that trigonally co-ordinated Cr^{2+} ions can form weak complexes with N_2O, CO_2, and C_2H_4 molecules also at room temperature. In this case the Cr^{2+} ions adopt a distorted tetrahedral co-ordination. At 150 °C the adsorption of O_2 and N_2O is dissociative, with formation of Cr^{4+} ions by oxidation of Cr^{2+}. The Cr^{4+} ions have an approximately tetrahedral co-ordination consisting of three oxygen atoms from the zeolite skeleton and one from the adsorbate. This latter oxygen atom can react with CO at 300 °C, thus re-establishing the initial valency and co-ordination state of the chromium ions.

A detailed study of type Y zeolites containing Cr^{2+} ions (prepared by exchange with a solution of $CrCl_2.4H_2O$) has been reported from our laboratory[8]. Dehydration of these zeolites at temperatures up to 500 °C was not accompanied by breakdown of the crystal structure for degrees of exchange up to 70%. The following results were obtained with samples in which the degree of exchange was 14%. The optical spectrum of the zeolite dried in a vacuum at room temperature had an absorption band at 13 500 cm^{-1}, characteristic of octahedrally co-ordinated Cr^{2+} complexes. Dehydration at 500 °C causes this band to split into two (12 200 and 16 200 cm^{-1}) as a result of a change in symmetry of the co-ordination sphere and of the formation of co-ordinationally unsaturated Cr^{2+} ions. Dehydration also causes replacement of the water ligands by oxygen from the zeolite skeleton, as shown by the shift of the charge-transfer absorption peak from 38 000 to 30 000 cm^{-1}. Adsorption of water or ammonia re-establishes the octahedral co-ordination of the Cr^{2+} ion. The formation of weak ethylene complexes at room temperature was also reported. The accessibility of the Cr^{2+} ions in dehydrated zeolites to various adsorbed molecules suggests that these ions are stabilised in S_{II} or $S_{II'}$ sites.

We also showed[8] that the redox properties of the Cr^{2+} ions in dehydrated zeolites are different from those of the same ions in solutions or on the surface of SiO_2. The co-ordinationally unsaturated Cr^{2+} ions in dehydrated zeolites are more stable in an oxygen atmosphere, and their valency is not changed by adsorption of oxygen at room temperature. The only effect of oxygen adsorption is the formation of weak complexes between O_2 molecules and Cr^{2+} ions, characterised by maxima in the optical spectrum at 12 000, 16 600, 18 300, 21 200, 28 000, and 31 000 cm^{-1}.

4. Manganese

The electronic structure of the ground state of the atom is $(A)(3d)^5(4s)^2$. Only bivalent manganese ions have been introduced into zeolites by ion exchange. Since the intensity of the d–d absorption bands of the Mn^{2+} ions is low, optical methods of investigation have not been widely used. On the other hand, manganese-containing zeolites have been studied in depth by ESR because the ESR signals from Mn^{2+} ions can be observed over a wide range of temperature and concentration.

The ESR work published up to 1972 is described in detail in Ref.1. That work established the existence of Mn^{2+} ions in zeolites in different co-ordination states, but it left unresolved a number of inconsistencies in the treatment of the experimental results.

More recent work on manganese-containing zeolites was reported by Tikhomirova and coworkers[16–20] and by Taranukha and coworkers[21–24]. The samples examined contained, in addition to manganese ions, the cations Li, K, Cs, Mg, Ca, Co, Sr, Ba, La, or Y. The Mn^{2+} ions, introduced to an extent of 0.05–2 ions per elementary cell, were used as paramagnetic probes.

Tikhomirova and coworkers[16–20] studied manganese-containing zeolites of types Y and A. The ESR spectra were measured at Q band (35 GHz). The localisation sites of the Mn^{2+} ions were identified from the change in g-factor and from the splitting between the central components of the hyperfine structure, and also from the width of the first and the sixth component, which allowed the different spectra to be clearly distinguished. Measurements on manganese-containing sodalite and erionite (in which hexagonal prisms are absent) gave, for the first time, pure ESR spectra which could be assigned with full confidence.

By analysing the spectra of samples before and after dehydration these workers concluded that in type Y zeolite ion migration occurs in the direction large hole → $S_{II}(S_{II'})(O_h)$ → $S_{II}(S_{II'})(T_d)$ → $S_{I'}$ → S_I, and in the opposite direction during hydration[20]. The adsorption of ammonia, pyridine, and some other molecules also causes Mn^{2+} ions to migrate along the zeolite skeleton.

It was also noted that the changes in the ESR spectra accompanying dehydration and the adsorption of various molecules are very sensitive to the nature of the second cation present in the zeolite. Thus, in the dehydration of CaY and CdY zeolites these cations effectively block the S_I sites and impede the penetration of manganese ions. In the MgY zeolite a significant fraction of the Mn^{2+} ions can find its way into S_I sites, and in ZnY all the S_I sites are occupied

by manganese ions. These results are explained[20] by postulating a heat of dehydration of the Mn^{2+} ions greater than that of Ca^{2+} and Cd^{2+} ions but smaller than that of Mg^{2+} and Zn^{2+} ions. Since the S_I sites are accessible only to ions which have lost the whole of their co-ordinated water they should be occupied, in the first instance, by the ions with the lowest heat of hydration, as is found in practice.

The existence in type Y zeolites of Mn^{2+} ions in octahedral, distorted octahedral, tetrahedral, and lower symmetry configurations has been confirmed by ESR and by optical and luminescence spectroscopy[21-24].

5. Iron

The electronic structure of the ground state of the atom is $(A)(3d)^6(4s)^2$. Relatively few studies of iron-containing zeolites by ESR have been reported, and none by optical spectroscopy. The first publication[25] on this topic described a study by ESR and magnetic susceptibility measurements, showing that dehydration of the ammonium form of a type Y zeolite (10^{-2} at.% Fe) produces ferromagnetic structures with $g_{eff} = 2.4 \pm 0.1$ and $\Delta H = 1600$ Oe. It was assumed[25] that the diameter of the ferromagnetic particles is less than 20 Å, and their composition is $Al_{3-x}Fe_xO_4$ (where $x \leq 3$).

Other work[26,27] on iron in zeolites has relied on ESR and luminescence methods. The Na and NH_4 forms of zeolite Y and mordenite (0.1 wt.% Fe) were studied in this way. The initial zeolites contained isolated Fe^{3+} ions in tetrahedral co-ordination, as shown by the ESR spectra ($g_{eff} = 4.3$) and the luminescence spectra. As the zeolites are dehydrated at temperatures up to 600 °C the ESR signal is gradually suppressed, and the ESR spectra of the dehydrated ammonium forms of both zeolite types develop a broad signal with $g_{eff} \cong 2.3$ which is ascribed to the formation of ferromagnetic particles. In the Na forms a weak signal from ferromagnetic particles is observed only from the type Y zeolite dehydrated at temperatures above 500 °C. This behaviour is explained[26,27] in terms of the deficit of Na^+ ions in the type Y zeolite ($Na^+ : Al^{3+} = 0.97$).

The ESR method has been used also to study FeNaY zeolites containing Fe^{3+} ions introduced from a solution of $FeCl_2$ (27% exchange)[28]. The ESR spectrum immediately after exchange was almost indistinguishable from that of the initial NaY zeolite, and consisted of a single broad line. Dehydration led to the appearance of a signal with $g \cong 4.31$, whose intensity increased with the dehydration temperature. This signal was assigned[28] to Fe^{3+} ions in a co-ordination "substantially" different from octahedral". By using the molecular probe method it was concluded that the Fe^{3+} ions are localised in $S_{I'}$ ($S_{II'}$) sites.

Ref. 29 describes a study of iron-containing type Y zeolites prepared by exchange with an iron thiocyanate solution. The ESR spectra obtained after exchange include a signal from Fe^{3+} ions in a distorted octahedral configuration with $g \cong 3.75$. Heat treatment of the samples in a stream of He at 550 °C lowered the width of the signal by a factor of 2 without affecting the g-factor, which the authors ascribe to changes in both the relative position and the immediate surroundings of the Fe^{3+} ions. Heating the samples in a hydrogen–nitrogen mixture at 350 °C (the temperature of incipient reduction of the iron) produces a signal with $g = 2.04$ ($T_{meas} = -196$ °C) which is assigned to Fe^{2+} ions. Reduction in the same atmosphere at 550 °C causes the formation of metallic iron and the appearance of ferromagnetism. By comparing the ESR results with those of nuclear gamma-resonance (NGR) (i.e. Mössbauer) spectroscopy the authors conclude that in this gas mixture the transition from Fe^{3+} to Fe^0 takes place through the Fe^{2+} state in the range 350–550 °C. They also showed that the crystal structure of the iron-containing zeolites is distorted in the reduced samples.

The interactions of adsorbed NO and NO_2 molecules with bivalent iron ions in NaY zeolites and in mordenite have been studied[30] by ESR and i.r. spectroscopy. Two types of nitrosyl $Fe(I)NO^+$ complexes, differing in the effective spin number ($S = 3/2$ and $S = 1/2$), were detected. The high-spin complexes are formed by the adsorption of nitric oxide at pressures of several Torr, and are characterised by the parameters $g_\perp = 4.07$ and $g_\parallel = 2.003$. When samples containing high-spin complexes are treated in a vacuum at 25–100 °C this ESR signal is gradually replaced by a new signal with $g_1 = 2.015$, $g_2 = 2.055$, $g_3 = 2.089$, produced by the low-spin complexes. The complexes are formed by the interaction of the NO molecules with Fe^{3+} ions, involving the transfer of the unpaired electron from the molecule to the cation. The adsorption of NO_2 molecules on these zeolites leads to oxidation of the Fe^{2+} ions to Fe^{3+} ions (in a distorted tetrahedral co-ordination). The ESR spectra contain, in addition to the signal from these ions, a characteristic triplet with $g = 2.005$ and $A = 56$ Oe, assigned to NO_2 molecules vibrating in the zeolite holes. Since the samples used in that work[30] had been reduced in hydrogen the possibility of a breakdown in their crystal structure[29] must be borne in mind.

An extensive investigation by Krzyzanowski[31-36] of Fe-containing type Y zeolites revealed that the Fe^{2+} ions are easily oxidised to Fe^{3+} in oxygen. Though the main theme of that work was the formation of radicals during the adsorption of unsaturated hydrocarbons and benzene on cerium-containing zeolites, FeY zeolites were shown to have very similar properties in respect to radical formation. Kinetic measurements by the ESR method led to a mechanism of radical formation involving the transfer of an electron from the oxygenated adsorbed species to the organic molecule. In the case of FeY zeolites these species are diamagnetic, and their structure is thought to be O_x^{2-}, where $x = 2$ and (or) 1.

Paramagnetic forms of adsorbed oxygen have been observed on reduced iron-containing FeNaHY zeolites: O_2^- anion radicals and oxygen-containing particles stable up to 500 °C whose structure has not been established[37]. Even small amounts of iron (≤0.07 wt.%) added to NaHY and LiY zeolites have been shown to induce the formation of these oxygen radicals following oxygen adsorption, the Fe^{2+} ions acting as electron donors.

6. Cobalt

The electronic structure of the ground state of the atom is $(A)(3d)^7(4s)^2$. Whereas very few papers on cobalt-containing zeolites had been published when the previous review[1] was written, in recent years these systems have attracted much attention. Klier[38,39] has extended his early work[1] on CoNaA zeolites, and has shown that in the hydrated zeolites the Co^{2+} ions are located in large holes as the $[Co(H_2O)_6]^{2+}$ hexa-aquo complexes, giving an absorption band at 19000 cm^{-1} in the optical spectrum. Dehydration of the zeolites causes localisation of the Co^{2+} ions at the centres of triangles of oxygen ions forming the windows of cubo-octahedra (S_{IA} sites). The adsorption of cyclopropane, olefin, and acetylene molecules causes complex formation between these molecules and the Co^{2+} ions: the complexes have a distorted

tetrahedral co-ordination consisting of three oxygen ions from the zeolite skeleton and one adsorbed molecule. The adsorption of ammonia and water molecules is accompanied by complex formation followed by a change in co-ordination in the sequence triangle → tetrahedron → octahedron, depending on the amount of adsorbate present.

An ESR study of CoNaA zeolites is reported in Refs. 40 and 41. The dehydrated zeolites at 4.2 K give a signal with $g_{\parallel} = 2.003$ and $g_{\perp} = 5.7$, consistent with localisation of the Co^{2+} ions in a trigonal co-ordination (S_{IA} sites). The hydrated zeolites give a signal with $g_{\parallel} \cong 2.2$ and $g_{\perp} \cong 5.1$, assigned to hexa-aquo cobalt complexes in large zeolite holes. We should note that data on the localisation of Co^{2+} ions in dehydrated type A zeolites obtained by ESR and optical spectroscopy methods agree with X-ray structural studies[42] of these zeolites, according to which the Co^{2+} ions are localised near the centres of the entry windows of the cubo-octahedra, with a slight shift (0.16 Å) from the plane of the window towards the centre of the hole.

There is general agreement[43–48] that the cobalt ions in hydrated X and Y zeolites are present as $Co(H_2O)_6^{2+}$ complexes in the large holes. Upon dehydration of the CoX zeolites the Co^{2+} ions acquire a tetrahedral co-ordination, and become stabilised in S_{II}, SII', or SI' sites[43–46], whereas in CoY zeolites the ions are either tetrahedrally co-ordinated[45–47] or octahedrally co-ordinated (in S_I sites)[48] and inaccessible to adsorbed H_2O and NH_3 molecules at room temperature[45,46].

A detailed comparative study of the properties of A, X, and Y zeolites containing Co^{2+} ions, carried out by reflectance u.v. spectroscopy and ESR, is described in Ref. 49. Under specified conditions the ESR spectra of Co^{2+} ions in the zeolites could be observed at 77 K and above. It was shown that A, X, and Y zeolites differ in their ability to stabilise the Co^{2+} ions, depending on the dehydration conditions, and this was ascribed to the difference in polarisability of the zeolite lattice for different Si/Al ratios. Thus, differences can be detected even in the hydrated zeolites: in type A zeolites the $Co(H_2O)_6^{2+}$ complexes interact with the zeolite lattice, whereas in X and Y zeolites they are relatively free. Tetrahedrally co-ordinated Co^{2+} ions are formed in type Y zeolites under dehydration conditions more rigorous than in types A and X.

Dehydration of zeolite A under mild conditions (110 °C, 12 h, helium stream) leads to stabilisation of the Co^{2+} ions in six-sided windows (S_{II} sites) to give tetrahedral $Co(Ox)_3 . H_2O$ complexes. As the dehydration temperature is raised to 600 °C the ions migrate to SI' or SII' sites, forming $Co(Ox)_3OH^-$ or $Co(OX)_3O^{2-}$ complexes, where Ox is an oxygen atom from the zeolite skeleton and OH^- and O^{2-} are residual fragments of H_2O molecules. On the other hand dehydration of X and Y zeolites at 600 °C leads to the formation of both tetrahedral $Co(Ox)_3O^{2-}$ complexes (in SI' or SII' sites) and of octahedral $Co(Ox)_6$ complexes (in S_I sites). We note that the reported[49] stabilisation of Co^{2+} ions with a tetrahedral co-ordination in strongly dehydrated type A zeolites is inconsistent with reports[38–42] that Co^{2+} is stabilised in a trigonal co-ordination after drastic dehydration. This discrepancy may be due in some measure to differences in the sample activation conditions: Heilbron and Vickerman[49] dehydrated their materials in a stream of helium, whereas most other workers have used vacuum dehydration. Differences in the heating rate of the samples may also have had some effect.

Measurements of the optical spectra of Co-containing A, X, and Y zeolites are reported also in Ref. 50. It is concluded that the Co^{2+} ions in dehydrated CoNaA zeolite have a trigonal co-ordination, whereas in CoNaX and CoNaY samples these ions adopt both tetrahedral and octahedral co-ordinations.

The adsorption of various molecules on dehydrated A, X, and Y zeolites containing Co has attracted much attention. We have already mentioned a study[39] of the adsorption of olefins and acetylene on CoNaA zeolite. The adsorption of alkane and alkene hydrocarbons (ethylene, propene, but-1-ene, and pent-1-ene) has been studied, by optical spectroscopy, also in CoNaX zeolites, which are catalytically active towards olefin oxidation[44]. The optical spectra were found to be unaffected by alkane hydrocarbons, whereas the adsorption of alkenes distorts the co-ordination sphere of the tetrahedral Co^{2+} complexes.

The adsorption of various nitrogen-containing molecules has been studied by two groups of workers[45,51–55]. Adsorption of ammonia leads to the formation of octahedral complexes. Adsorption of methyl isocyanide on CoCaY zeolite at room temperature[51,52] produces the five-co-ordinated $Co(CH_3NC)_5^{2+}$ complexes, which are converted (in the presence of an excess of methyl isocyanide) into the six-co-ordinated $Co(CH_3NC)_6^{2+}$ complexes, with ESR spectral parameters $g_{\parallel} = 2.003$, $g_{\perp} = 2.172$ and $g_{\parallel} = 2.008$, $g_{\perp} = 2.087$ respectively. Adsorption causes the Co^{2+} ions to migrate into large zeolite holes, where the complexes are formed.

Lunsford and coworkers[53–55] found that the Co^{2+} complexes formed in the large holes of CoNaY zeolites by the adsorption of amines interact with oxygen to give O_2^- anion radicals in the co-ordination sphere of the cobalt ion: $[Co(III)L_xO_2^-]^{2+}$, where $L_x = NH_3$, CH_3NH_2, and $C_3H_7NH_2$. In the case of NH_3 and CH_3NH_2 storage of the zeolites at 20 °C for 10–15 h produces also the binuclear complexes $[L_xCoO_2^-CoL_x]^{5+}$. The ESR spectral parameters of both types of oxygen adduct are similar to those of the analogous complexes in solution.

Some of the most recent publications describe studies by u.v. and ESR spectroscopy of the localisation sites of Co^{2+} ions in natural zeolites (montmorrillonite[56] and clinoptilolite[57]). The conclusion was that, as in type X and Y zeolites, dehydration leads to the formation of tetrahedrally co-ordinated Co^{2+} ions. In clinoptilolite trigonal co-ordination of the ions is also possible.

7. Nickel

The electronic structure of the ground state of the atom is $(A)(3d)^8(4s)^2$. All the studies of zeolites containing nickel(II) so far reported have been by optical spectroscopy. The earliest work[58–60] was on the state of the Ni^{2+} ions in type A zeolites (see Ref. 1). Further developments of that investigation are reported in Refs. 61–63. The observed[61,62] migration of Ni^{2+} ions from large holes into S_{IA} sites upon dehydration of the type A zeolites is consistent with the conclusions from earlier work[58–60].

Studies of X and Y zeolites[61–63] have shown that Ni^{2+} ions present in the large holes as hexa-aquo complexes after exchange will gradually migrate, during dehydration, into S_{II} sites (up to 200 °C), then into SII' and SI' sites, and lastly into S_I sites (at 500 °C), where they are stabilised in a distorted octahedral co-ordination (with adsorption bands at ~10000, 16000, and ~22000 cm^{-1}). These conclusions on the stabilisation of Ni^{2+} ions in S_{IA} sites (A zeolites) and in S_I sites (X and Y zeolites) are consistent with results obtained by X-ray diffraction analysis[64,65].

The diffuse reflectance spectra of type Y zeolites have revealed[66,67] in addition to isolated ions, aggregates of Ni^{2+} ions. The degree of aggregation of the ions was shown to

be very sensitive to the exchange conditions. In the absence of hydrolysis of the salt used for ion exchange different types of isolated Ni^{2+} ions are detected, localised in different sites, depending on the concentration of the ions and on the heat treatment conditions of the zeolite. If the ion-exchange salt is partially hydrolysed the nickel ions are incorporated in the zeolite as polynuclear hydroxo complexes, yielding aggregates of nickel ions when the samples are heated. The bridging oxygen of these aggregates (Ni–O–Ni) does not belong to the zeolite skeleton. The aggregates of nickel ions give a charge-transfer absorption band at a lower frequency than the isolated ions.

In addition to the work on nickel-containing A, X, and Y zeolites, one paper has been published on NiL zeolite[68]. In this work the nickel ions were found to take up two co-ordination states as the dehydration temperature was raised. In the first of these states the nickel is bound to the zeolite skeleton through the residual water molecules, whereas in the second state (observed for dehydration temperatures above 300 °C) the Ni^{2+} ions are co-ordinated directly to the skeleton. As the temperature is raised above 100 °C the Ni^{2+} ions become gradually more accessible to water and ammonia molecules adsorbed from the gas phase.

The adsorption on NiA, NiX, and NiY zeolites dehydrated at temperatures up to 500 °C of strongly polar molecules such as water (at room temperature) and pyridine (at 200 °C) causes inverse migration of the Ni^{2+} ions from S_I (or S_{IA}) sites into large holes[61,62]. In the case of pyridine the planar complexes $[Ni(Py)_4]^{2+}$ are formed, with absorption bands at ~10 000, 16 000, ~20 000, and ~25 000 cm^{-1}. Adsorption of NH_3 on zeolites dehydrated at temperatures up to 200 °C leads to the formation of ammine complexes of the Ni^{2+} ions. On the other hand no complex formation is observed on zeolites dehydrated at higher temperatures[63]. This is explained by pointing out that the Ni^{2+} ions in S_I and S_{IA} sites (unlike those in $S_{I'}$ and $S_{II'}$ sites) are not accessible to ammonia molecules.

The adsorption of acetylene on type Y zeolite containing dehydrated or partially dehydrated Ni^{2+} ions causes reduction to the Ni^0 or Ni^+ state[69], and the Ni^+ ions react with acetylene to give $[Ni(C_2H_2)_n]^+$ complexes, where $n = 2, 3$. Complex formation between Ni^+ ions and acetylene or ethylene molecules was observed also on partially reduced X and Y zeolites[61]. By combining X-ray diffraction results with measurements of magnetic susceptibility the authors[61] were able to assign the Ni^+ ions which interact with alkene molecules to S_{II} (or $S_{II'}$) stabilisation sites.

The formation of Ni^+ ions has been observed also after reduction in H_2 or Co at 200–400 °C of nickel-containing NaA, NaX, NaY, NH_4A, NH_4X, NH_4Y, and CaNaY zeolites[70–73]. The concentration of Ni^+ ions was found to depend on the crystal structure type of the zeolite. In NiCaNaY zeolites[71,72] two types of Ni^+ ions were detected, with different stabilisation sites and characterised by ESR spectra with $g_\perp = 2.09$, $g_\parallel^1 = 2.48$, and $g_\parallel^2 = 2.80$. Adsorption of O_2 produced an ESR spectrum from the O_2^- anion radical ($g_1 = 2.045$, $g_2 = 2.008$, $g_3 = 2.0015$), whereas in an NO atmosphere the Ni^+ ions were oxidised to the bivalent state. The interaction of Ni^+ ions with CO produces the $Ni(CO)_2^+$ and $Ni(CO)_3^+$ complexes[72,73].

The adsorption of NO on nickel-containing zeolites is discussed in Refs.74–76. The interaction between NO molecules and Ni^{2+} is shown to lead to the formation of a charge-transfer complex in which the nickel ions initially occupy S_I positions but are subsequently transferred to $S_{I'}$ positions. The adsorption of NO and NO_2 is discussed also in Ref.15: as in the chromium-containing samples, mentioned above, the $[Ni^+NO^+]$ and $[Ni^+NO_2^+]$ complexes, which have identical ESR spectra, were detected ($g_\perp = 2.169$ and $g_\parallel = 2.33$).

8. Copper

The electronic structure of the ground state of the atom is $(A)(3d)^9(4s)^2$. Copper is particularly convenient for ESR and optical spectroscopy studies, and therefore many publications on copper-containing zeolites have appeared since the last review[1]. The more recent work has largely resolved the inconsistencies noted in the earlier review[1].

Refs.77 and 78 discuss copper-containing type A zeolites. Hydration of CuNaA and CuLiA zeolites was found to produce tetrahedral complexes of Cu^{2+} ions with one water molecule and three oxygen anions from the zeolite lattice as ligands, located near the hexagonal windows (S_{IA} sites). It was also found that hydration of Ca^{2+}- and Mg^{2+}- substituted type A zeolites causes migration of the Cu^{2+} ions into the large holes, where hexa-aquo complexes can be accommodated. A study[79] of the effect of copper content on the ESR spectra of type A zeolites has shown that electronic exchange interaction between the copper ions sets in when the copper content reaches one ion for every seven elementary cells, and this leads to the appearance of a new signal (in addition to the signal from isolated ions): a somewhat distorted singlet ~120 Oe wide.

The localisation sites of Cu^{2+} ions in type X zeolites are discussed in Refs.80–84. Kenzi and coworkers[80] examined, by ESR, samples of CuNaX containing 1.9 Cu^{2+} ions per elementary cell, and found that the copper ions migrate during dehydration and become stabilised in S_{III}, S_{II} (or $S_{II'}$), and $S_{I'}$ sites at 70–200 °C, whereas at 400 °C they penetrate into S_I sites. Localisation of Cu^{2+} ions in S_I sites during dehydration is reported also in Ref.81, but these results should be accepted with caution because the samples were exposed to an atmosphere of butene at 200 °C, followed by oxygen at the same temperature, before the measurements. In an extension of this work[82] the authors point out that Cu^{2+} ions become strongly bound to the zeolite skeleton even for dehydration temperatures as low as 80–100 °C. ESR measurements at 77 K revealed three distinct signals, corresponding to stabilisation of the copper ions at different locations in the skeleton (S_{III}, S_{II}. and $S_{II'}$). After dehydration at 120–200 °C a substantial fraction of the copper ions is localised in $S_{II'}$ sites, and raising the dehydration temperature to 400 °C causes migration of the ions to S_I sites. However, as the authors themselves point out[82], additional evidence is needed to confirm these conclusions.

Vansant[83] does not discuss the stabilisation sites of Cu^{2+} ions specifically, but he points out that in dehydrated zeolites these ions are co-ordinated by three lattice oxygens, suggesting localisation in $S_{II}(S_{II'})$ or $S_{I'}$ sites. Lastly, Peigneur and coworkers[84] also mention S_{II} and $S_{II'}$ sites as possible localisation positions in the zeolite X skeleton.

Most of the work on copper ions has been done with type Y zeolites. Changes in ESR spectra similar to those described in Ref.1 have been observed[85] after dehydration of CuNaY zeolites, though in this case there was no decrease in the intensity of the ESR signal after dehydration at 400 °C. This difference is apparently due to the oxidising treatment (O_2, 400 °C) to which the sample were subjected after dehydration. Turkevich and coworkers[86] reported, in addition to the signals described in the previous review[1], a symmetrical signal with $g \cong 2.17$ whose intensity increased with the degree of exchange. They ascribed this signal to cluster

formation without defining the cluster structure. Cluster formation is reported also by Mörke and coworkers[87], who studied the state of copper ions in CuNaY zeolites (9–64% exchanged) dehydrated at 200–600 °C. A substantial fraction of the copper ions was found to be localised in S_I, $S_{I'}$, and $S_{II'}$ sites, and it was noted that cluster formation is favoured not only by an increase in the degree of exchange but also by an increase in the dehydration temperature. Reports of the localisation of copper ions in S_{III} and S_{II} sites of hydrated zeolites were confirmed by Soria and coworkers[88], and the localisation in $S_{I'}$ and $S_{II'}$ sites after dehydration of the zeolites at 400–600 °C was confirmed by X-ray structural analysis[89]. The stabilisation of copper ions in S_I sites was further confirmed by Jacobs and coworkers[90], who pointed out that the ease with which the copper ions are reduced depends on the localisation sites of the ions.

Cu^{2+} ions stabilised in S_I, $S_{I'}$, and $S_{II'}$ sites can form ion pairs of various types at high degrees of exchange[91–94]. The stabilisation of copper ions in S_I and $S_{I'}$ sites has been shown[94] to be influenced by the heating rate of the zeolite during dehydration. Thus, for a heating rate of 1.7 K min^{-1} the Cu^{2+} ions can be localised in hexagonal prisms, but an increase in the heating rate to 25 K min^{-1} prevents the ions from entering those sites. This effect can explain the slight discrepancies which still exist between the conclusions of different workers on the ability of copper ions to be stabilised in S_I sites of type Y zeolites.

Investigations by optical spectroscopy[95,96] also suggested the possibility of forming copper ion pairs at high degrees of exchange. Again, S_{III} sites were found to be the preferred stabilisation point of Cu^{2+} ions in the hydrated zeolites. Dehydration at gradually increasing temperatures initially causes migration to S_{II} and $S_{II'}$ sites (100–300 °C), followed by migration to S_I and $S_{I'}$ sites (300–600 °C).

Extensive studies[66,67,97–103] of the effect of exchange, dehydration, and redox conditions on the state of copper ions in type Y zeolites have been carried out by ESR, i.r., and optical spectroscopy methods. The stabilisation sites of isolated copper ions identified by this work agree, on the whole, with conclusions from earlier work. The suggested formation of "strong" or "weak" associations of copper ions, differing in the intensity of the spin–exchange interaction, is interesting. The "weak" associations are assumed to have characteristics similar to those of isolated copper ions localised in S_{III} and S_{II} sites, whereas the "strong" associations differ very substantially from isolated ions: they are formed by heat treatment under oxidising conditions of the clusters arising from the hydrolysis of the copper ions in the zeolite holes during exchange at pH 8–9. The "strong" associations are thought to be bridging structures of the M–O–M type, including non-lattice oxygen.

Many recent publications discuss the adsorption of ammonia, pyridine, and other nitrogen-containing molecules on copper-substituted zeolites. The interest in this type of investigation appears to stem from the specificity of the resulting complexes, which makes it very easy to identify them by ESR and optical spectroscopy.

The ESR method has been used[104] to study the adsorption of ammonia and pyridine on CuNaY zeolite, and the formation of the square coplanar complexes $[Cu(NH_3)_4]^{2+}$ and $[Cu(Py)_4]^{2+}$ has been demonstrated (ESR spectral parameters $g_\parallel = 2.25$, $g_\perp = 2.04$, $A_\parallel = 175$ Oe, and $g_\perp = 2.03$, $g_\parallel = 2.24$, $A_\parallel = 185$ Oe respectively). Vacuum heat treatment at 100 °C did not affect the spectrum of a sample on which pyridine had been adsorbed, whereas inversion of the g-factors occurred in the sample on which ammonia had been adsorbed ($g_\perp = 2.26$, $g_\parallel = 2.03$). The inversion was produced by removal of the ammonia molecules and by the resulting change in the symmetry of the co-ordination sphere to that of a tetrahedron compressed along the trigonal axis. It was also found that in the case of samples containing adsorbed pyridine a change in measurement temperature from room temperature to −196 °C does not affect the ESR spectra. Hence the authors suggest[104] that the $[Cu(Py)_4]^{2+}$ complexes are formed within the sodalite cells, which "freezes" the motions of the complex and makes the spectral parameters independent of the measurement temperature.

Further developments in this work have also been reported. It was shown[83] that the behaviour of Cu^{2+} ions towards the adsorption of pyridine and ammonia is substantially the same in types Y and X zeolites, and also[86] that the specific adsorption of pyridine (unlike that of ammonia, which interacts with copper ions even at room temperature) is limited to temperatures above 120 °C. This difference is most probably due to the inability of pyridine molecules to penetrate into the sodalite cells except at high temperatures.

An ESR study of the adsorption of ammonia on CuNaY zeolite as a function of the amount of ammonia adsorbed is described in Ref. 98. Four types of complex were shown to be formed, differing in the number of ammonia molecules (five, three, and two) and in their disposition in the co-ordination sphere.

Optical spectroscopy has shown[66] that the adsorption of NH_3 on dehydrated zeolites leads to the formation of di- and tri-ammines (absorption maximum at ~15 200 cm^{-1}), with a very small number of tetra-ammines (shoulder at 17 000 cm^{-1}). Adsorption of pyridine produces di- and tetra-pyridine copper complexes (15 400 and 17 200 cm^{-1}), whereas the adsorption of large quantities of ammonia[105] produces mainly tetra-ammines (16 500 cm^{-1}). Partial desorption of the ammonia leads to the formation of complexes to which the structure $(O)_3$–Cu–NH_3 has been assigned.

Thus, whereas in the case of pyridine adsorption the structural information given by optical spectroscopy is consistent with the ESR results, pointing to the formation of $[Cu(Py)_4]^{2+}$ complexes, there is some disagreement between the two methods in determining the structure of the copper ammine complexes. The ESR measurements indicate preferential formation of the $[Cu(NH_3)_4]^{2+}$ complex [for example, Lunsford and coworkers[94] failed to detect any other ESR signals, even at very low levels of adsorption ($N_{NH_3}/N_{Cu^{2+}} \ll 1$)], whereas the optical spectra suggest that these complexes are formed only when the zeolites are saturated with ammonia.

Vansant and Lunsford[91] studied the adsorption of ammonia, methylamine, and ethylamine molecules on CuNaY zeolite. Ammonia adsorption was found to give rise to complexes containing four ammonia molecules and having the D_{4h} square coplanar symmetry, whereas only one adsorbate molecule entered into the co-ordination sphere of the copper ion after adsorption of the amines. It is interesting to note that two types of complex between copper ions and amines were detected in the sodium form of the zeolite, whereas in the calcium form only one complex was found. The difference in structure between the two types of complex in CuNaY probably involves differences in the stabilisation sites of the copper ions ($S_{II'}$ or $S_{I'}$).

Interesting results were obtained in an extensive investigation by optical spectroscopy of the adsorption of ammonia, pyridine, and ethylenediamine molecules from aqueous solutions on CuNaY zeolite[46,96,106]. The following copper ion complexes were detected: $[Cu(NH_3)(H_2O)_5]^{2+}$, $[Cu(NH_3)_2 \cdot (H_2O)_4]^{2+}$, $[Cu(NH_3)_6]^{2+}$, $[Cu(Py)_4]^{2+}$, and $[Cu(en)_3]^{2+}$. On the other hand, after adsorption of ethylenediamine from the gas phase[84] the complexes $[Cu(en)]^{2+}$ and $[Cu(en)_2]^{2+}$

have been detected by ESR and u.v. spectroscopy. [Cu.$(en)_3]^{2+}$ complexes were formed only after lengthy exposure of the sample to ethylenediamine.

The adsorption of molecules not containing nitrogen has not been studied in such detail. Leith and Leach[82] examined, in addition to the adsorption of ammonia and pyridine, also the adsorption of butene, cyclopropane, and 3,3-dimethylbutene, and they showed that the latter molecules interact with Cu^{2+} ions in S_{II} positions whereas NH_3 and pyridine molecules can interact with Cu^{2+} ions in S_I positions.

A study by ESR and i.r. spectroscopy of the interaction within zeolites between carbon monoxide molecules and copper cations in different states has been reported[99,101]. Isolated copper ions were found not to interact with CO up to 500 °C, whereas the weak magnetic associations of these ions form complexes with CO at low temperatures and oxidise it to CO_2 at temperatures above 300 °C (being reduced to Cu^{2+} by this reaction). These processes are thought to involve non-lattice oxygen. The stronger associations of copper ions, which include a bridging oxygen atom not belonging to the zeolite skeleton, oxidise the CO molecules to CO_2 and to carbonates even at low temperatures.

We should note that the ESR method can be used also to study complex formation between adsorbed molecules and univalent copper ions. The adsorption of nitric oxide on Cu^+–Y zeolites prepared by reduction of zeolites containing copper(II) has been studied in this way[85,107], and the formation of the Cu^+–NO complex has been observed ($g_\parallel = 1.89$, $g_\perp = 2.009$). The results of various studies of the complexes of copper and some other transition metals (Co, Cr, Ni, Fe) with nitrogen-containing molecules are discussed in detail in Refs.108 and 109.

III. IONS OF THE METALS FROM THE SECOND AND THIRD TRANSITION PERIODS

Relatively few papers on studies by ESR and optical spectroscopy of zeolites containing ions from the second and third transition period have been published. As far as the present writers are aware, all of them are concerned with ions from Group VIII of the Periodic Table.

1. Ruthenium

The electronic structure of the ground state of the atom is $(K)(4d)^7(5s)^1$. Ruthenium-containing type Y zeolites have been studied[110] by ESR and optical spectroscopy, and the properties of the ruthenium ions were shown to be very sensitive to the exchange conditions and to the subsequent treatment of the samples. Thus, samples exchanged in an excess of ammonia gave signals from Ru^{3+} complexes differing in the number of ammonia ligands ($g_1^A = 2.57$, $g_2^A = 2.20$, $g_3^A = 1.73$, and $g_1^B = 2.44$, $g_2^B = 2.12$, $g_3^B = 1.82$), whereas after exchange at pH ~7 only one broad band (with $g \approx 2.5$) is observed. Dehydration of the samples reduces some of the ruthenium to the metal with formation of ferromagnetic micro-crystals of an alloy of ruthenium with the iron present as an impurity in the zeolites. The formation of these micro-crystals is indicated by the appearance of a very strong ESR signal at low fields. The size of the micro-crystals depends on the exchange conditions (increasing with pH). In very finely divided crystals the adsorption of hydrogen molecules has a marked effect on the ferromagnetic properties, as shown by the substantial decrease in signal strength.

The preparation of ruthenium zeolites of types A, X, and Y by exchange methods is discussed also in Ref.111.

2. Rhodium

The electronic structure of the ground state of the atom is $(K)(4d)^8(5s)^1$. Rhodium-containing X and Y zeolites (2–80% exchange) have been studied by ESR.[110,112–114]. In type X zeolites exposed to an oxidation (O_2, 500 °C) and a reduction treatment (H_2, 150 °C) in succession, ESR signals from Rh^{2+} ions in a distorted octahedral co-ordination have been observed[110]. The adsorption of various molecules (O_2, NO, Co, NH_3) at room temperature had no effect on the ESR spectrum (i.e. complex formation was not observed). This observation, together with the co-ordination of the Rh^{2+} ions, suggests that these ions are localised in S_I sites.

Unlike the type X zeolites, in which only isolated Rh^{2+} ions are observed, type Y zeolites give rise to paramagnetic centres after an oxidising treatment ($g_\perp = 2.69$, $g_\parallel = 2.18$, $A_1 = 355$ Oe, $A_2 = 110$ Oe). These centres consist of two non-equivalent rhodium ions (called an ion pair[112]). Integral intensity measurement indicates that ~20% of the rhodium ions take part in ion pair formation.

Rhodium pairs have been shown[112–114] to act as adsorption centres for various molecules (H_2O, NH_3, O_2, CO, NO, etc.). Adsorption of water molecules causes the formation of paramagnetic associations in the large holes of the zeolite, containing at least four rhodium atoms. Storing the samples in an ammonia atmosphere at room temperature or at 100 °C also produces changes in the ESR spectra, resulting from the interaction of the rhodium pairs with ammonia.

The adsorption of CO, O_2, and NO molecules, unlike the adsorption of strongly polar molecules, leads to the formation of unstable complexes which break down under evacuation even at room temperature. The adsorption of CO molecules was found[113] to produce complexes giving an ESR signal with the parameters $g_\perp = 2.186$, $g_\parallel = 1.992$, and $A_\parallel(Rh) = 18.5$ Oe. By using labelled carbon monoxide (^{13}CO) it was shown that only one CO molecule is present in each complex, and that this molecule is covalently bound to the rhodium.

The adsorption of NO at 77 K causes the formation of nitrosyl complexes whose composition includes two molecules of nitric oxide[114].

The formation of complexes of the peroxy type following oxygen adsorption has been observed ($g_\perp = 1.943$, $g_\parallel = 2.014$). These species (called σ-complexes) were found to be very reactive towards the oxidation of various molecules, including alkenes and hydrogen[110,112].

An ESR study of the properties of rhodium ions in NaY zeolite is described also in Ref.115. In the early stages of the thermal activation of the zeolite in oxygen (at ~100 °C) the tervalent rhodium complexes $[Rh(NH_3)_5Cl]^{2+}$ initially introduced by ion exchange are found to break down, giving the paramagnetic bivalent rhodium complexes $[Rh(NH_3)_5]^{2+}$ whose ESR spectra have the parameters $g_1 = 2.09$, $g_2 = 2.06$, and $g_3 = 1.97$. At higher temperatures (500 °C) Rh^{2+} ions directly attached to the zeolite skeleton are formed. As in our experiments[112,113], these workers observed the formation of complexes with CO and O_2, but their structural interpretation is somewhat different from ours. They assume that oxygen-containing complexes are produced by the oxidation of diamagnetic Rh^+ ions, giving the bridge structure Rh^{2+}–O–O–Rh^{2+}. However, in view of the small distance between the paramagnetic Rh^{2+} ions in this structure, which should lead to substantial interaction between the unpaired electrons, we would expect the ESR spectrum to be more complex than the spectrum actually observed (charateristic of the systems with $S = 1/2$). For these reasons we consider the proposed bridge structure to be improbable.

3. Palladium

The electronic structure of the ground state of the atom is $(K)(4d)^{10}$. All the work on palladium-containing zeolites reported so far has been done on samples prepared by ion exchange between type Y zeolites and solutions of tetra-ammine complexes of bivalent palladium ions.

Naccache and coworkers[116,117] examined by ESR the state of the palladium ions and its dependence on various treatments of the sample (including the adsorption of hydrogen and carbon monoxide molecules). Oxidising treatments were shown to produce a signal in the ESR spectra of the zeolites with the parameters $g = 2.233$, $\Delta H = 16$ Oe, assigned to Pd^{3+} ions in a distorted octahedral or trigonal co-ordination (S_I or $S_{I'}$, S_{II} sites). Adsorption of hydrogen at room temperature on an oxidised sample reduced the Pd^{3+} ions to Pd^{+}, whose ESR signals have the parameters $g_\perp = 2.10$, $g_\parallel = 2.28$ and $g_\perp = 2.11$, $g_\parallel = 2.41$ respectively. It is pointed out that ~8% of the palladium ions give rise to ESR signals. The suggested localisation of the palladium ions in $S_{I'}$ sites is confirmed by X-ray diffraction results[118], which indicate that 10.6 of the 12.5 palladium ions in the elementary cell are located in $S_{I'}$ sites.

The adsorption of CO on these samples causes the appearance of an ESR signal with the parameters $g_1 = 2.192$, $g_2 = 2.061$, and $g_3 = 2.038$. By using carbon monoxide enriched in the ^{13}C isotope the components of the signal for each g-factor were shown to be split into three ($A_1 = 56$ Oe, $A_2 = 56$ Oe, and $A_3 = 60$ Oe). Hence the authors concluded[116,117] that the Pd^{+} ions form complexes with two CO molecules.

An ESR study of the adsorption of NO molecules on PdNaY zeolite is reported in Ref. 119. A signal with $g = 1.95$ was observed on oxidised as well as on reduced samples, leading to the conclusion (confirmed by i.r. spectral measurements) that the complexes formed by the Pd^{2+} ions contain one molecule of NO.

Garbowski and coworkers[120,121] reported a study of PdNaY zeolite by optical spectroscopy. Most of the spectra were complex, and had to be analysed by resolving the absorption lines into their components. The conclusion was that in the initial samples the Pd^{2+} ions were present as $[Pd(NH_3)_4]^{2+}$ complexes in the large zeolite holes, whereas after dehydration at 500 °C in a stream of oxygen the Pd^{2+} ions were converted into the C_{3v} co-ordination[122]. The same workers examined the adsorption of ammonia, pyridine, water, and nitric oxide molecules. From their optical measurements they concluded that the adsorption of water gives two types of complex: tetrahedral, in $S_{I'}$ sites, and square coplanar, in large holes. The adsorption of NO molecules led to the formation of complexes containing one molecule of nitric oxide. A study[121] of the simultaneous adsorption of CO and NO showed that these complexes can be of two types: one type (in $S_{I'}$ sites) does not interact with CO, whereas the other (in $S_{II'}$ sites) can co-ordinate an additional CO molecule to give a complex of composition $Pd(O)_3NOCO$.

IV. CONCLUSIONS

To conclude this review we shall mention an important paper by Sancier and Inami[122], who studied by ESR the reduction in hydrogen at 400 °C of Pd^{2+}NaY and Pd^{2+}CaNaY zeolites containing also iron ions. These workers noted the formation, under these conditions, of reduced forms of iron, whereas no reduction took place in zeolites not containing palladium. The effect is explained by postulating the formation (during the reduction of palladium ions) of atomic hydrogen, which subsequently migrates towards the iron ions and reduces them (the "spill-over" effect).

Our discussion of work by ESR and optical spectroscopy on zeolites containing ions of the transition elements leads to the following general conclusions. Evidently, these methods do not always allow the localisation sites of the ions in the zeolites after dehydration to be identified unambiguously, but they provide reliable data on the accessibility of the ions to adsorbed molecules of various types. The dehydration of zeolites containing ions of the transition elements is usually followed by gradual migration of the ions into S_{II}, $S_{II'}$, $S_{I'}$, and S_I sites. However, the effect is strongly dependent on the dehydration conditions and on the nature of the cation. Thus, the localisation of cations in S_I sites of faujasites is clearly observed only when low heating rates are used.

For these reasons the "centre of gravity" of the research in this area has been shifted from the determination of the localisation sites of ions in zeolites to the study of the electronic structure and of the properties of the complexes formed in the zeolite holes by the interaction of the transition metal ions with adsorbed molecules. In these complexes the ions of the transition elements often form a bond with both the adsorbed molecule and the oxygen ions from the zeolite skeleton, and their co-ordination, localisation site, and even valency can change as a function of the nature of the ligands, the concentration of adsorbed molecules, and the temperature. Another area which has attracted attention in recent years is the identification and study of ions in "unusual" valency states, which can often be stabilised in zeolites by interaction with the alumino-silicate skeleton. ESR and optical spectrosocpy methods offer a high sensitivity and a high information content, and allow these processes to be monitored even when other methods fail.

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Singlet Oxygen: Methods of Preparation and Detection

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An historical account of the discovery of singlet oxygen is given, its physicochemical properties are discussed, and existing methods of preparation and detection are reviewed. 171 references.

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I. INTRODUCTION

15 years ago singlet oxygen was either unknown to most chemists or treated as a spectroscopic state of theoretical interest in the physics of the upper atmosphere. In recent years, however, singlet oxygen has come to the notice of a wide range of researchers. It was shown to have a high reactivity towards many organic compounds, to play an important role in the chemistry of atmospheric pollution, to be involved in the degradation of organic materials by light and oxygen, to take part in the life processes of plants and animals, to behave as a carcinogen, etc.

The first papers dealing specifically with singlet oxygen appeared in the mid-1960's, and by the year 1970 the number of such publications was over 100. According to Kasha and Khan[1] all our views on the participation of molecular oxygen in various chemical and biological systems must now be reconsidered from the standpoint of our new understanding of singlet molecular oxygen. In the Soviet literature very little has been published so far on singlet molecular oxygen. In 1965 Arbuzov referred to singlet oxygen in a review[2] of the oxidation of organic compounds, and a more recent review[3] mentions the quenching of singlet oxygen in the context of the resistance to photo-oxidation of organic compounds. The foreign literature contains a number of reviews dealing with various aspects of the singlet molecular oxygen problem[1,4-15]. In the present review we shall discuss the nature of singlet oxygen and the methods by which it can be prepared and detected.

In Fig.1 the ground state of the oxygen molecule is shown as an energy level diagram[13,16], illustrating the formation of molecular orbitals (MO) following the close approach of two oxygen atoms. Each oxygen atom has eight electrons. Four of these remain in $\sigma(1s)$ and $\sigma^*(1s)$ orbitals, while the next four move into $\sigma(2s)$ and $\sigma^*(2s)$ orbitals. The next six electrons move into three bonding MO: $\sigma(2p_x)$, $\pi(2p_y)$, and $\pi(2p_z)$. The last pair of electrons can be accommodated either on one of the π^* orbitals (if the electrons have opposite spins) or on two MO [$\pi^*(2p_y)$ and $\pi^*(2p_z)$] if the spins are parallel. The latter variant is energetically preferred, because of the large repulsion energy between two electrons in the same orbital: the two electrons are further apart when in different orbitals, and their mutual repulsion is less marked. This preferred electronic configuration is illustrated in Fig.1.

This state of the oxygen molecule is known as the triplet sigma-state ($^3\Sigma$). The higher-energy configuration, in which the last two electrons are located in the same $\pi^*(2p_y)$ orbital, is shown in Fig.2. It corresponds to the lower excited state of the oxygen molecule, which is a singlet state because the electrons are paired. This state of the oxygen molecule is denoted as $^1\Delta$ and lies 22.5 kcal mole^{-1} above the $^3\Sigma$ ground state (Table 1). This energy level was obtained by emission spectroscopy[17], the $^1\Delta \rightarrow {}^3\Sigma$ transition corresponding to a wavelength of 1269 nm (0.9772 eV). The next excited state of the oxygen molecule is 37.5 kcal mole^{-1} above the ground state[17] and has the electronic configuration shown in Fig.3: it is denoted by the symbol $^1\Sigma$. It differs from the $^3\Sigma$ state in that the last two electrons in the π^* orbitals have antiparallel spins in the $^1\Sigma$ state. In terms of group theory and of the theory of symmetry properties these three states of the oxygen molecules can be described as $^3\Sigma_g^-$, $^1\Delta g$, and $^1\Sigma_g^+$ respectively. Some of the characteristics of these three states are listed in Table 1.

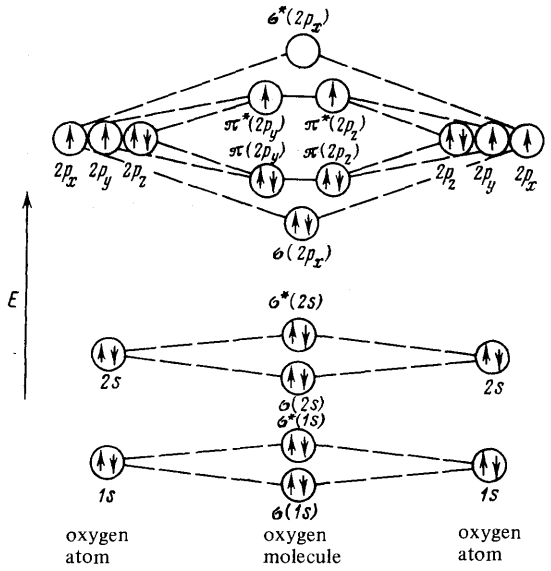


Figure 1. Normal (or triplet) $O_2(^3\Sigma_g^-)$.

The photochemical reactions of organic compounds with molecular oxygen were studied in detail in the first half of the present century. Some of these reactions are of the utmost importance in biological terms. For example, it was shown that some endoperoxides can regenerate an oxygen molecule when heated. Thus red rubrene gives a colourless peroxide when exposed to light in the air, but on being heated it becomes red again and begins to fluoresce[18]. The formal

analogy between this type of reaction and the reversible absorption of oxygen by hemoglobin is evident.

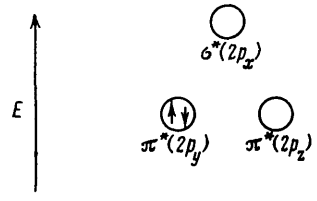


Figure 2. Singlet $O_2(^1\Delta_g)$.

Table 1. Lowest electronic states of an oxygen molecule, and their properties[1].

Electronic state	Life time, s		Relative energy, kcal mole^{-1}	Position of the 0.0 band, λ, nm	Equilibrium internuclear distance, A
	vacuum	solution			
$^1\Sigma_g^+$	7	10^{-11}	37.51	762.14	1.227
$^1\Delta_g$	2700	10^{-6}	22.53	1268.7	1.216
$^3\Sigma_g^-$	∞	∞	0	—	1.207

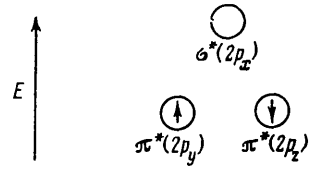


Figure 3. Singlet $O_2(^1\Sigma_g^+)$.

The classical work of Kautsky[19] in the 1930's demonstrated that photo-excitation of a sensitiser in the presence of oxygen can cause oxidation of an organic molecule physically removed from the sensitiser. He concluded that the light energy absorbed by the sensitiser (dye) is transferred to the oxygen (by fluorescence quenching of the dye) which is thus converted from its ground triplet state into one of the excited singlet states ($^1\Delta$ or $^1\Sigma$). The singlet oxygen then attacks the organic molecule, giving the oxidation product[19]. Thus Kautsky's mechanism can be summarised as

$$\begin{aligned} S &\xrightarrow{h\nu} {}^1S \\ {}^1S &\rightarrow {}^3S \\ {}^3S + {}^3O_2 &\rightarrow S + {}^1O_2 \\ {}^1O_2 + A &\rightarrow AO_2 \ . \end{aligned} \qquad (1)$$

Direct energy transfer from the sensitising dye to the organic molecule can be excluded, because the absorption bands of many organic molecules lie at wavelengths shorter than those of the dyes used as sensitisers, and therefore the energy of the excited dye molecules is insufficient to raise these acceptors into their excited states[14].

In the 1940's Terenin generalised Kautsky's model by pointing out that the total electron spin is conserved in this process. He described the energy transfer process as follows[20,21,106]:

$$S[\uparrow][\uparrow] + O_2[\downarrow][\downarrow] \rightarrow \tilde{S}[\uparrow\downarrow][\ ] + {}^1O_2[\uparrow\downarrow][\ ]$$

where the symbol ~ denotes an excess of vibrational energy.

However, Kautsky's mechanism was not accepted by most of the leading foreign workers, and for many years singlet oxygen remained of interest only to astrophysicists and to specialist gas kineticists. However, the situation changed in 1960 when Seliger[22] discovered a red luminescent emission on mixing H_2O_2 and HClO. The spectrum of this radiation, which had been first reported by Mallet 33 years previously[23], was found to consist of a narrow band at 634 nm.

Khan and Kasha[24,25] confirmed Seliger's results and observed an additional band at 703 nm. The separation of these two bands (1567 cm^{-1}) agrees within experimental error with the vibrational frequency of molecular oxygen in the ground state (1580 cm^{-1}); furthermore, the O–O bond in the hydrogen peroxide molecule was shown to remain undisturbed by the reaction

$$H_2O_2 + HClO \rightarrow O_2 + HCl + H_2O \ . \qquad (2)$$

On these grounds the authors ascribed[24,25] this radiation to an excited state of molecular oxygen. Though this assignment was later shown[26] to be only partly correct (see below), Khan and Kasha had correctly associated the luminescence with metastable, excited, singlet oxygen. Following this assignment, Kautsky's hypothesis was more widely accepted.

The same two bands were observed[26] in the radiation from a stream of gaseous oxygen exposed to an electric discharge. The chemiluminescence of the H_2O_2–HClO system was re-examined, and in addition to the bands at 634 and 703 nm a new, weak band was discovered at 762 nm, corresponding to the transition $O_2(^1\Sigma) \rightarrow O_2(^3\Sigma)$, as well as a stong band at 1270 nm, corresponding to the transition $O_2(^1\Delta) \rightarrow O_2(^3\Sigma)$.[27] Obviously, the bands at 634 and 703 nm must have the same origin whether the luminescence is produced in solution or in a gas discharge.

It has been suggested[10,26] that the bands at 634 and 703 nm are produced by a dimer consisting of two excited $O_2(^1\Delta)$ molecules, which are deactivated simultaneously and emit a single quantum of energy:

$$2O_2(^1\Delta) \rightarrow 2O_2(^3\Sigma) + h\nu \ . \qquad (3)$$

This transition produces radiation at 634 nm if both molecules of the product are in the vibrational ground state: if one of the product molecules is in the first vibrational level the radiation will be at 703 nm.

The hypothesis of simultaneous electronic transitions was not novel. The absorption bands at 634 and 580 nm in liquid oxygen, which are responsible for its blue colour, had previously been assigned to double transitions of the same type, in which the absorption of one photon causes the simultaneous transfer into excited states of two electrons in two different molecules[28,29]:

$$2O_2(^3\Sigma) + h\nu \rightleftarrows 2O_2(^1\Delta)$$

Thus, the hypothesis put foward by Arnold and coworkers[26] is consistent with earlier reports. The band at 634 nm is convenient for monitoring the concentration of $O_2(^1\Delta)$ singlet oxygen, because its intensity is proportional to the square of the concentration of $O_2(^1\Delta)$ (thus confirming the validity of the hypothesis). In addition to the double transition (3), the following transitions have also been proposed[10,26]:

$$2O_2(^1\Sigma) \rightarrow 2O_2(^3\Sigma) + h\nu_{861\,nm} + h\nu_{861\,nm}$$

$$2O_2(^1\Delta^1\Sigma) \rightarrow 2O_2(^3\Sigma) + h\nu_{478\,nm} \qquad (4)$$

All these dimers are assumed to be simple collisional complexes.

Thus singlet oxygen was rediscovered in the reaction between H_2O_2 and HClO and in a stream of oxygen exposed to an electric discharge. It was later found[30] that the oxidation products of organic molecules exposed to the H_2O_2–NaOCl system are identical to those obtained by the sensitised oxidation of the same acceptors. Excited oxygen molecules generated in a discharge upstream from the organic solution have been shown[31] to react with various substituted anthracenes and alkenes to give oxidation products identical to those of the sensitised photo-oxidation of the same acceptors. These comparisons led to the conclusion that singlet oxygen is the reactive intermediate in sensitised photo-oxidation reactions, as originally suggested by Kautsky.

In a later variant of Kautsky's experiment the sensitiser and the oxygen acceptor were placed on opposite sides of a stearic acid film[32,33]. In spite of the 500 Å separation between the sensitiser molecules and the acceptor, sensitised photo-oxidation took place as a result of diffusion of the singlet oxygen molecules through the film.

Thus Kautsky's mechanism is now universally accepted. On the other hand, up to the mid-1960's the Terenin–Schenck mechanism (called the Schenck mechanism in the foreign literature) was more widely used. Terenin[20,34] and (later) Schenk[35] proposed the following scheme for dye-sensitised photo-oxidation reactions

$$S \xrightarrow{h\nu} {}^1S$$
$${}^1S \rightarrow {}^3S$$
$${}^3S + {}^3O_2 \rightarrow [S \ldots O_2]$$
$$[S \ldots O_2] + A \rightarrow S + AO_2$$

where the metastable $[S...O_2]$ complex is the reactive intermediate which transfers oxygen to the acceptor A.

Following the demonstration[30,31] that singlet oxygen is the active intermediate in many sensitised photo-oxidations, interest in the Terenin–Schenck mechanism began to wane, but there was still no proof that a long-lived complex (as postulated in that mechanism) was not formed as a precursor of the free, singlet molecular oxygen. This important problem has been finally resolved by comparing the effectiveness of oxygen quenching of the fluorescence of pyrene excimers under low- and high-intensity irradiation respectively (using light from a nitrogen laser[36]). Under high irradiation intensity each oxygen molecule can produce 200 excited pyrene excimers, the fluorescence quenching being comparable (~91%) with the quenching observed at very much lower irradiation intensities (93%). In order to explain this effect we have to assume that each O_2 molecule has sufficient mobility to quench ~100–200 pyrene molecules, and therefore that the life time of the pyrene–oxygen complex is less than 2×10^{-10} s. These experiments exclude the possibility of complex formation between an excited pyrene molecule and oxygen, and they also exclude the existence of any excited formation (including oxygen) having a life time greater than 2×10^{-10} s.

A theoretical study of the energies of different states of the $(S...O_2)$ complex has shown[14,37] that though the $({}^3S + {}^3O_2)$ complex corresponds to a weak minimum ($\leq$300 cm^{-1}) this state has a very short life time ($<10^{-10}$ s due to its fast relaxation into lower-lying dissociative states of the complex: $[S...O_2({}^1\Delta)]$ and $[S...O_2({}^1\Sigma)]$, giving $O_2({}^1\Delta)$ or $O_2({}^1\Sigma)$. Obviously, the oxide complex is too short-lived to act as an intermediate responsible for oxygen transfer in sensitised photo-oxidation reactions. Additional evidence against the existence of oxide complexes was provided by measurements[38] of the decomposition kinetics of the endoperoxide of diphenylfuran, aimed at explaining whether oxygen transfer to other oxygen acceptors A occurs by the direct bimolecular reaction

$$DPFO_2 + A \rightarrow AO_2 + DPF$$

or with the participation of a singlet oxygen molecule

$$DPFO_2 \rightarrow DPF + {}^1O_2$$
$${}^1O_2 + A \rightarrow AO_2.$$

In these equations $DPFO_2$ is a molecule of diphenylfuran endoperoxide, A is an oxygen acceptor molecule (tetramethylethylene, cyclohexa-1,3-diene, or rubrene), and DPF is a molecule of diphenylfuran. The results convincingly favour the second mechanism (i.e. the singlet oxygen mechanism).

II. METHODS OF PREPARATION OF SINGLET OXYGEN

Singlet oxygen can be prepared by physical or by chemical methods. The physical methods of preparative value include photo-sensitisation and radio-frequency discharge. Among the chemical methods the most important are the decomposition of hydrogen peroxide by hypochlorite or hypobromite and the decomposition of some ozonides.

1. Formation of Singlet Oxygen in Photo-processes

a) Photo-sensitisation

Photo-sensitised oxidation occurs by the following scheme[39]:

$${}^1S_0 + h\nu \xrightarrow{k_1} {}^1S_1 \text{ (absorption)}$$
$${}^1S_1 \xrightarrow{k_2} {}^1S_0 + h\nu' \text{ (fluorescence)}$$
$${}^1S_1 \xrightarrow{k_3} {}^1S_0 \text{ (internal conversion)}$$
$$\left.\begin{aligned} {}^1S_1 &\xrightarrow{k_4} {}^3S_1 \\ {}^3S_1 &\xrightarrow{k_5} {}^1S_0 \end{aligned}\right\} \text{(intercombination conversion)}$$
$$\left.\begin{aligned} {}^1S_1 + {}^3O_2 &\xrightarrow{k_6} {}^1S_0 + {}^1O_2 \\ {}^3S_1 + {}^3O_2 &\xrightarrow{k_7} {}^1S_0 + {}^1O_2 \end{aligned}\right\} \begin{array}{l}\text{(energy transfer; formation}\\ \text{of singlet oxygen)}\end{array}$$
$${}^1O_2 \xrightarrow{k_8} {}^3O_2 \text{ (deactivation of singlet oxygen)}$$
$${}^1O_2 + {}^1A_0 \xrightarrow{k_9} {}^1(AO_2)_0 \text{ (formation of product)}$$

In these equations ${}^1S_0$, ${}^1S_1$, and ${}^3S_1$ are the singlet ground state, the singlet excited state, and the triplet excited state of the sensitiser S, ${}^1A_0$ and ${}^1(AO_2)_0$ are the singlet ground states of the organic molecule A and of the product AO_2, and ${}^3O_2$ and ${}^1O_2$ are the triplet state and the singlet excited state of oxygen (${}^3\Sigma$; ${}^1\Sigma$, and (or) ${}^1\Delta$ respectively).

One of the most important conclusions from studies of dye-sensitised photo-oxidation reactions is that singlet oxygen molecules can be obtained by energy transfer from the sensitiser molecules in excited triplet or singlet states[6–9]. The mechanism of the energy transfer process is assumed to involve intermediate formation of a contact pair between the sensitiser and the oxygen molecule[14,39,40] (Fig. 4). Since the ground state of the organic molecule is singlet, and that of the oxygen is a triplet ${}^3\Sigma$ state, the ground state of the contact pair (or weak complex) $S...O_2$ must be triplet[40]. Excitation of S or of O_2 produces a series of excited states of the complex: some possibilities are illustrated in Fig. 4. In addition to these states of the complex we have to consider states involving charge transfer (CT), formed by the transfer of an electron from S to O_2. For example, for the benzene–O_2 complex the charge transfer complex lies approximately

100 kcal mole^{-1} above the ground state[41]. The next lower excited state of the contact pair is the *F*-state[1,3,5], which can transfer oxygen[4] and from which transitions into the three repulsive states $^3G_0$, $^1X_1$, and $^1X_2$ can be expected. These transitions give oxygen in the ground triplet state and in two singlet states ($^1\Delta$ and $^1\Sigma$) respectively.

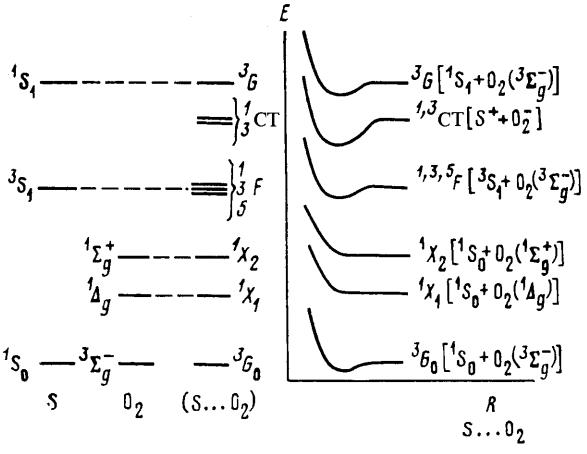


Figure 4. Energy level diagram and potential energy curves for the sensitiser, the oxygen, and the sensitiser–oxygen pair.

Quenching of triplet states by oxygen. Various mechanisms have been proposed to explain the oxygen quenching of molecules in the triplet state[19,42,43]. An analysis[14] of the energy level diagram (Fig.4) was based on the following processes for the quenching of molecules in the triplet state:

$$\begin{aligned}&(a)\ {}^1({}^3S_1+{}^3O_2)\rightarrow {}^1S_0+O_2({}^1\Sigma)\\&(b)\ {}^1({}^3S_1+{}^3O_2)\rightarrow {}^1S_0+O_2({}^1\Delta)\\&(c)\ {}^3({}^3S_1+{}^3O_2)\rightarrow {}^1S_0+O_2({}^3\Sigma)\end{aligned}\qquad(5)$$

The first two mechanisms were first suggested by Kautsky [see Ref.(1)], the third implies an enhancement of the intercombination transition in the S molecule resulting from interaction with the paramagnetic oxygen molecule. Although in principle this process can be assisted by the inhomogeneous magnetic field of the paramagnetic oxygen molecule[43], the effect has been shown[44] to be negligibly small. Furthermore, a study of the quenching of molecules in the triplet state by paramagnetic ions has shown[45] that the quenching efficiency is not correlated to the magnetic moment of the paramagnetic ions.

Another mechanism, proposed by Weiss[42], assumes electron transfer to the oxygen. In most cases this mechanism is excluded by energy considerations (see Fig.4), though it is quite probable in the case of molecules with a very low ionisation potential (amines) in a polar solvent[14].

Direct interaction between a triplet organic molecule and an oxygen molecule in the ground state is another possible quenching mechanism; however, it has been shown experimentally that even in the case of molecules undergoing photooxygenation this reaction is not involved in the quenching of the triplet molecules[14].

Calculations[46] for the aromatic hydrocarbon–oxygen contact pair, with an intermolecular distance of ~4 Å, clearly show that the transfer of energy to triplet oxygen, leading to the formation of $O_2(^1\Sigma)$ or $O_2(^1\Delta)$ (see Eqns.5*a* and 5*b*), should be far more effective (100–1000-fold) than quenching in the ground state without energy transfer (Eqn.5*c*). This is because the process involving the conversion of the smallest amount of electronic energy into vibrational energy will be the predominant one: on the other hand, intercombination transitions always involve the conversion of the largest amount of electronic excitation energy into vibrational energy.

The following unimolecular rate constants have been calculated[40] for the quenching of a molecule in the triplet state having an energy $E_T = 60$ kcal mole^{-1}:

$^1F \rightarrow {}^1X_2$ (10^{12} s^{-1}; energy transfer to $O_2(^1\Sigma)$)
$^1F \rightarrow {}^1X_1$ (10^{11} s^{-1}; energy transfer to $O_2(^1\Delta)$)
$^3F \rightarrow {}^3G_0$ (10^9 s^{-1}; enhanced intercombination conversion).

The quenching of molecules in the triplet state by oxygen has been studied in the vapour[47–50], the liquid[51–54], and the solid phase[32,55–59]. Evidence that energy transfer to the oxygen is the basic mechanism of the oxygen quenching of triplet molecules has been obtained also by ESR: the quantum yield of the formation of singlet oxygen, which is proportional to the number of triplet molecules of naphthalene produced, was shown[60] by this technique to be ~1.

Since $^1O_2(^1\Sigma)$ has an excitation energy of 37.7 kcal mole^{-1} it can be produced by using sensitisers in which the energy of the triplet excited level is 37.7 kcal mole^{-1}, whereas $^1O_2(^1\Delta)$ can be obtained by energy transfer from any sensitiser of energy >22.6 kcal mole^{-1}. The ratio $O_2(^1\Sigma)/O_2(^1\Delta)$ has been studied[40] as a function of the triplet state energy of the sensitiser. It was found that the quenching of molecules with a high triplet state energy ($E_T > 50$ kcal) produces ~10 times more $O_2(^1\Sigma)$ than $O_2(^1\Delta)$. This is because a smaller amount of electronic energy is converted into vibrational energy by the creation of a $^1\Sigma$ (as compared to a $^1\Delta$) state. In the case of molecules having a triplet state energy <37 kcal only $^1\Delta$ molecules can be formed. For intermediate values of the triplet state energy of the sensitiser molecule ($50 > E_T > 37$ kcal) the ratio $O_2(^1\Sigma)/O_2(^1\Delta)$ falls smoothly to zero (Fig.5).[14]

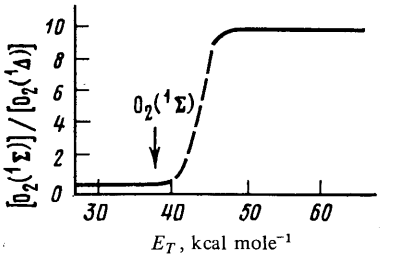


Figure 5. $O_2(^1\Sigma)/O_2(^1\Delta)$ ratio against the triplet state energy of the sensitiser.

Gollnick and coworkers[39] studied the triplet states of various types of sensitiser (dyes, aromatic hydrocarbons, carbonyl compounds). Electronic excitation of aromatic hydrocarbons and dyes give $^3(\pi,\pi^*)$ triplets, whereas carbonyl compounds (except naphthyl phenyl ketones[61] and fluorenone[62]) give $^3(n,\pi^*)$ triplets. As Table 2 shows, the triplet state energies of the sensitisers examined in that work[39] cover the range 30–85 kcal mole^{-1}.

Quenching of singlet states by oxygen (fluorescence quenching). It has long been recognised that oxygen can effectively quench the fluorescence of many organic molecules[63–68], but the mechanism of this effect was not understood. By applying theoretical calculations to the energy level diagram of the sensitiser–oxygen contact pair (Fig. 4) Kearns[14] concluded that relaxation of the excited organic molecule into a state with charge transfer (CT), i.e.

$$^1S_1 + {}^3O_2 \rightarrow (S^+ + O_2^-)$$

is the main mechanism involved in the oxygen quenching of molecules in an excited singlet state, and that the probability of quenching directly to the ground state is very much lower.

Table 2. Lowest triplet state energies of various photosensitisers[39].

Sensitiser	E_T, kcal mole^{-1}	Sensitiser	E_T, kcal mole^{-1}
Azulene	38—31	Pyrene	48.7
Anthracene	42.0	Propiophenone	74.6
Acetophenone	73.6	Rhodamine B	43
Bengal Rose	39,5—42,2	Tetrachlorofluorescein	42.2—44.1
Benzaldehyde	72.0	Tetrachloro-eosin (phloxin)	39.5—42.2
Benzene	84.5	Tetracene	29.4
Benzophenone	68.5	Thioxanthone	65.5
1-Bromonaphthalene	59.0	Triphenylene	66.6
Biphenyl	65.7	Phenanthrene	62.2
Carbazole	70.1	Flavone	62.0
Xanthone	74.2	Fluorene	67.6
Methylene Blue	34	Fluorenone	53.3
Naphthalene	60.9	Fluorescein	45.2—48.1
1-Naphthyl phenyl ketone	57.5	Quinoline	62.0
2-Naphthyl phenyl ketone	59.6	Eosin	43.2—46.0
		Erythrosin	43.1—45.8

The importance of CT states is confirmed, for example, by the much higher (100-fold) effectiveness of NO in quenching the singlet states of hexafluoroacetone[69], since NO has a higher electron affinity than oxygen.

The oxygen quenching of the fluorescence of aromatic hydrocarbons is diffusion-controlled in solution as well as in the vapour phase[69–78].

Generation of singlet oxygen by sensitisers on a solid substrate. A new method of photo-oxygenation, described by Blossey and coworkers[79], relies on the generation of singlet oxygen by a photosensitiser supported on an insoluble polymeric substrate. The sensitiser Bengal Rose was bonded to chloromethylated polystyrene through its carboxyl and (or) phenolic groups. A suspension of sensitiser-coated polymer spheres in a suitable solvent (CH_2Cl_2, $CHCl_3$, CCl_4, C_6H_6, CS_2, etc.) containing the organic compound was irradiated in the presence of molecular oxygen. The photo-oxidised product was isolated simply by filtering off the sensitiser spheres and removing the solvent by evaporation. From these experiments the authors concluded[79] that free singlet oxygen is formed with high efficiency by energy transfer from the polymer–Bengal Rose system to the oxygen. The usual problems of photo-sensitised oxydation (solubility of the sensitiser, and its separation, bleaching, regeneration, etc.) are avoided by the use of a heterogeneous method of photo-oxygenation. The sensitiser bonded to the polymer can be re-used without significant loss of effectiveness. Other (related) sensitisers on a polymer substrate were also examined (eosin, fluorescein, chlorophyllin, and hematoporphyrin), but their quantum efficiency towards the singlet oxygenation process was found to be lower than that of Bengal Rose.

Ion-exchange resins, which form strongly bound complexes with ionic sensitisers, can also be used as the solid substrate[80]. Thus, the anionic dyes Bengal Rose and eosin have been introdued into the strongly basic Amberlite IRA-400 anion exchange resin, and the cationic dye Methylene Blue into the strongly acidic Amberlite IRC-200 cation exchange resin. The sensitisers supported on a resin, like those supported on a polymer, act as effective heterogeneous photo-oxidation catalysts.

Following Kautsky's experiments, Nielsson and Kearns[81] developed several heterogeneous sensitisers with an absorption bond. They found that silica gel covered with Bengal Rose or Methylene Blue, or alumina covered with pyrene, offer the same (albeit low) photo-sensitisation efficiency as the corresponding homogeneous systems.

Triphenylmethane dyes are reported[82] to be inactive as sensitisers in solution, but to become active when bound to polymers or used in a solid environment.

An interesting solid-phase, thin-film photochemical singlet oxygen generator has been described[83]. It consists of a water-cooled tube internally coated with a thin solid film of the sensitiser (Bengal Rose), irradiated with a tungsten lamp, and a flask coated with a film of solid rubrene, which acts as a trap for singlet oxygen. An opaque screen separates the tube from the flask so as to avoid self-photosensitised oxidation of the rubrene. The choice of rubrene as a trap was dictated by its high reactivity towards $^1O_2$ coupled with total inactivity towards $^3O_2$, and also by its low volatility. Passing a stream of dry air through the whole system at 3 mmHg for 24 h converted 65% of the rubrene into rubrene peroxide. The reaction was monitored spectroscopically (in benzene, at 494 and 530 nm). However, the reproducibility of the results obtained with singlet oxygen generated by this method is not high[83].

Photo-sensitised generation of singlet oxygen by near infra-red radiation. The generation of $^1O_2$ by irradiation with near infra-red light ($\lambda < 0.9$ μm) from a xenon lamp was first reported by Nathan and Adelman[84], who used the following sensitisers: 1,1′-diethyl-2,2′-tricarbocyanine iodide, xenocyanine, and 3,3′-diethyl-9,11,15,17-dineopentylene-thiapentacarbocyanine iodide. No singlet oxygen was obtained when other sensitisers were used. The reactions were carried out in dioxan and dichloroethane solutions, using 9,10-dimethylanthracene as the acceptor (which was converted into the 9,10-endoperoxide). The progress of the reaction was monitored by the intensity of the 9,10-dimethylanthracene absorption bands at 245 and 265 nm, which are not given by the endoperoxide.

b) Formation of singlet oxygen through charge transfer complexes

This mechanism for the formation of singlet oxygen was proposed after an investigation[85,86] of the reversible absorption of u.v. light (230–400 nm) by olefin–oxygen collision complexes.

Reversible absorption by olefins and aromatic hydrocarbons in the u.v. region, due to the presence of oxygen, has been observed repeatedly in the liquid and the gas phase[43,44,87–93], and was studied in detail in our laboratory[94,95] (see Ref. 95 for a detailed bibliography on this effect). This work led to the firm conclusion that any

compound able to act as an electron donor towards oxygen (aromatic and heterocyclic hydrocarbons, alkenes, and alkanes) can form a charge transfer complex (CTC) with oxygen in which the hydrocarbon acts as an electron donor and the oxygen as the acceptor. As a result, these hydrocarbons show additional absorption in the u.v. or visible region in the presence of oxygen, consisting of a very strong band in the shorter-wave region and much weaker (~100 times) bands in the longer-wave region. The stronger band is due to absorption with charge transfer (between the hydrocarbon and the oxygen), and the weaker bands to singlet–triplet absorption by the hydrocarbon induced by the oxygen (which is forbidden by the selection rules under normal conditions). The spectrum of the original hydrocarbon is shifted towards longer wavelengths by this additional absorption.

Collisions between hydrocarbon molecules (donor, D) and oxygen molecules (acceptor) produce weak complexes (contact pairs) which have a triplet character[86]:

$$^1D_0 + O_2(^3\Sigma) \rightleftarrows {}^3[D \ldots O_2(^3\Sigma)].$$

This complex can absorb light. The result is the transfer of an electron to the acceptor (oxygen) with formation of a charge-transfer complex which can be either in the triplet or in the singlet state, since both D^+ and O_2^- are in doublet states:

$$(a)\ {}^3[D \ldots O_2(^3\Sigma)] \xrightarrow{h\nu} {}^3[D^+ - O_2^-]$$

$$(b)\ {}^3[D \ldots O_2(^3\Sigma)] \xrightarrow{h\nu} {}^1[D^+ - O_2^-]. \qquad (6)$$

In reaction (6a) both the ground state and the CT state are triplet, which makes the transition allowed according to the spin conservation rule.

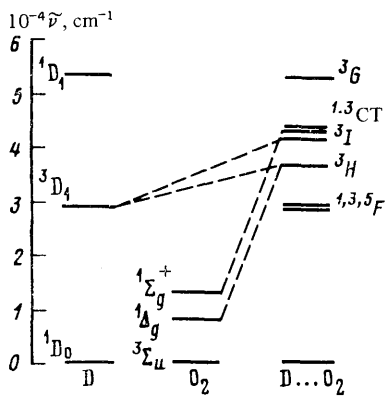


Figure 6. Energy level diagram for the donor, the oxygen, and their 1 : 1 contact pair.

The first excited singlet and triplet states of the donor and of the corresponding 1 : 1 pairs with oxygen in the ground state $O_2(^3\Sigma)$ are $^1D_1$, $^3D_1$, and ^3G, $^{1,3,5}F$ respectively (Fig. 6). The donor molecule in the first excited singlet state $^1D_1$ forms a CTC in the triplet state ^3G with oxygen in the ground state, whereas a donor molecule in the $^3D_1$ state can give quintet (^5F), triplet (^3F), and singlet (^1F) CTC states with oxygen in the ground state. If 1 : 1 pairs are formed between a triplet donor ($^3D_1$) and singlet oxygen in $^1\Delta$ or $^1\Sigma$ states, two additional states (denoted ^3H and ^3I) are created.

The CT state can interact with ^3G, obtaining its energy from the allowed transition between the ground and the singlet excited state of the donor. Similarly, ^3F can interact with ^{3}CT, thus borrowing energy from the CT transition and causing enhanced $S \rightarrow T$ absorption. It was shown[44] that the direct interaction between ^3F and ^3G states has a much weaker influence on the intensity of the $S \rightarrow T$ band than the interaction between the same states through a triplet state with charge transfer. Thus, the additional absorption observed consists of the allowed CT band, which borrows energy mainly from the allowed $^1D_0 \rightarrow {}^1D_1$ transition and also (to a much smaller extent) from the $S \rightarrow T$ band, which is strengthened by the ^{3}CT state. If this path for the internal conversion of energy from ^3G to ^3F through the ^{3}CT state is effective, the CTC in the ^3F state can produce a donor in the triplet state and molecular oxygen in the ground state:

$$^3[^3D_1 + O_2(^3\Sigma)] \rightarrow {}^3D_1 + O_2(^3\Sigma). \qquad (7)$$

An alternative mechanism includes the conversion of ^{3}CT into ^3I and ^3H states, which can then dissociate to give $^1O_2 + {}^3D_1$:

$$(a)\ {}^3CT \rightarrow {}^3I \rightarrow {}^3D_1 + O_2(^1\Sigma)$$

$$(b)\ {}^3CT \rightarrow {}^3H \rightarrow {}^3D_1 + O_2(^1\Delta). \qquad (8)$$

Reaction (7) gives singlet molecular oxygen by energy transfer from the triplet donor to the oxygen in the ground state (Kautsky's mechanism), whereas reaction (8) produces $^1O_2$ directly.

This mechanism for the formation of singlet oxygen is believed[86] to be very important in the chemistry of industrial atmospheric pollution.

c) *Direct optical excitation*

Liquid oxygen (and also gaseous oxygen at high pressure) has a series of bands in the u.v., visible, and i.r. region of the spectrum corresponding to various transitions (see above)[96,97]. The wavelength of the He–Ne laser (623.8 nm) corresponds almost exactly to the absorption band due to the $2O_2(^3\Sigma) \rightarrow 2O_2(^1\Delta)$ transition, and Evans[98] found that irradiation of a solution of 9,10-dimethylanthracene under a high oxygen pressure with light from a He–Ne laser causes photo-oxygenation of the anthracene (in the absence of a sensitiser). The quantum yield of the photo-oxidation was only 0.13, but it could be raised to ~0.6 by using a more reactive acceptor of singlet oxygen (1,3-diphenylisobenzofuran, DPBF). By using a range of different light sources Evans[98] established an approximate "action spectrum" for photo-oxidation by light of different wavelengths, and he showed that only light of wavelength corresponding to the known absorption bands of oxygen is active in promoting oxidation reactions. Though this method of generating singlet oxygen has little preparative value it is important in studies of the mechanism of various reactions involving singlet oxygen.

d) *Photolytic generation of singlet oxygen*

The photolysis of ozone is another method of producing $^1\Sigma$ and $^1\Delta$ oxygen in a gaseous system[99–104]:

$$O_3 + h\nu \rightarrow O_2[^1\Sigma \text{ or } {}^1\Delta) + O(^1D \text{ or } {}^3P).$$

From energy considerations we can establish the threshold

wavelengths for the direct production of $O_2(^1\Sigma)$ and $O_2(^1\Delta)$ by ozone photolysis. In principle the photolysis of ozone at $\lambda = 253.7$ nm can give either $O_2(^1\Sigma)$ or $O_2(^1\Delta)$ plus an atom of oxygen in the excited ^1D state, but in practice only $O_2(^1\Delta)$ is obtained[100]. Formation of $O_2(^1\Sigma)$ takes place by the following side reaction, involving energy transfer from an excited oxygen atom to molecular oxygen in the ground state[99,101,102,105]:

$$O(^1D) + O_2(^3\Sigma) \rightarrow O(^3P) + O_2(^1\Sigma).$$

The following reactions (which also take place in the system),

$$O(^1D) + O_2(^3\Sigma) \rightarrow O_2(^1\Delta) + O(^3P)$$
$$O_3 + h\nu_{253.7\,nm} \rightarrow O_2(^1\Sigma) + O(^1D)$$

are only minor sources of $O_2(^1\Delta)$ and $O_2(^1\Sigma)$.[100] It has been shown[14] that $O_2(^1\Sigma)$ can be obtained also by the photolysis of molecular oxygen from the reactions

$$O_2 + h\nu_{147\,nm} \rightarrow O(^1D) + O(^3P)$$
$$O(^1D) + O_2(^3\Sigma) \rightarrow O_2(^1\Sigma) + O(^3P).$$

2. Chemical Sources of Singlet Oxygen

a) Decomposition of hydrogen peroxide

The decomposition of hydrogen peroxide according to Eqn.(2) was used in the first definite demonstration of the participation of singlet oxygen in sensitised photo-oxidation reactions[30,107–109].

In the absence of organic compounds the resulting singlet oxygen is deactivated (with chemiluminescence) to triplet oxygen[107]. By comparing the chemiluminescence bands with the emission bands of gaseous oxygen in an electric discharge and with the absorption bands of liquid oxygen it was established that the decomposition of hydrogen peroxide gives a high yield of singlet oxygen molecules[24,25,107,108,110–112]. The chemiluminescence is produced by double molecular transitions [see Eqns.(3) and (4)] as well as by the single molecular transitions

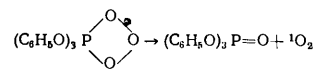
$$O_2(^1\Sigma) \rightarrow O_2(^3\Sigma) + h\nu_{760\,nm}$$
$$O_2(^1\Delta) \rightarrow O_2(^3\Sigma) + h\nu_{1270\,nm}. \qquad (9)$$

Studies of chemiluminescence[24,25,107,110] have yielded some other interesting results. Firstly, this work showed that the strongest band in the chemiluminescence spectrum (703.2 nm) results from a cooperative transition involving a pair of $O_2(^1\Delta)$ molecules, which is explained by the generation of large amounts of excited singlet oxygen during the decomposition of H_2O_2. Secondly, in solutions the chemiluminescence band at 760 nm [for the $O_2(^1\Sigma) \rightarrow O_2(^3\Sigma)$ transition] has a rotational fine structure which suggests that the radiation is from singlet oxygen molecules in gas bubbles[108] rather than from dissolved oxygen. Though the rotational structure has not been resolved in the other bands it is assumed that the whole of the radiation comes from oxygen molecules in the gas phase, because the life time of singlet oxygen in solution is very much shorter than in the gas phase (see Table 1).

The yield of singlet oxygen during the decomposition of hydrogen peroxide is very sensitive to the nature of the solvent[113]. In methanol the yield is 70%, and high yields are obtained also in ethanol and in a methanol–t-butanol mixture. In other solvents miscible with water the yield is usually <10%.[113] This effect is not understood at present. Since photo-sensitised oxygenation is not sensitive to the solvent it follows that the nature of the solvent can influence the formation of singlet oxygen but not its reactions[7].

b) Decomposition of ozonides

One of the most convenient methods of chemical generation of singlet oxygen is the decomposition of the adduct of triphenyl phosphite with ozone, which can be prepared at −70 °C. When heated to −35 °C this compound gives singlet molecular oxygen by the reaction[114–118]:



The proof of the formation of singlet oxygen by the decomposition of this adduct rests on the observation that various oxygen acceptors can be oxidised by it to give the same products as the recognised reactions of singlet oxygen with the same acceptors. Wasserman and coworkers[119] showed by ESR spectroscopy that the decomposition of this ozonide produces $O_2(^1\Delta)$, which could be detected in the gas phase after being evolved from the solution. However, the possibility of complicating side reactions was later pointed out[120]. Tetramethylethylene (TME) was found to react with triphenylphosphiteozone at −60 °C, i.e. below the temperature at which the rate of decomposition of the adduct is sufficient to produce free oxygen in substantial amounts. Furthermore, by comparing the reactions of this adduct with TME and with 2,5-dimethylfuran (another effective acceptor of singlet oxygen) we note that TME is the more effective acceptor towards this adduct whereas in the sensitised oxidation reactions the opposite is true.

This work[120] led to the conclusion that direct transfer of O_2 from triphenylphosphiteozone (by an alternative mechanism) must be possible. The mechanism yields the same products as the reaction with free singlet oxygen, but it has a different selectivity towards various organic compounds. The study was extended to other alkenes[121], and direct transfer of O_2 from the adduct to the acceptor was again observed. In this sense the ozonides are very similar to the molecular oxides of Terenin and Schenck's mechanism[14,20,34,35].

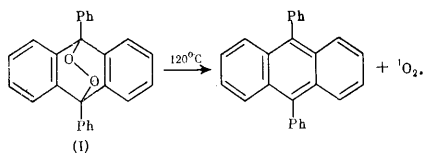
The ozonides of 4-ethyl-2,6,7-trioxa-1-phosphabicyclo-[2,2,2]octane[122] and 1-phospha-2,8,9-trioxa-adamantane[123] have also been used as sources of singlet oxygen, which they generate at somewhat higher (and more convenient) temperatures.

c) Decomposition of endoperoxides

Various aromatic hydrocarbons (especially linear polyacenes) undergo sensitised photo-oxidation reactions in the presence of oxygen to give endoperoxides which dissociate on heating, regenerating the initial hydrocarbon and free molecular oxygen[9,124]. Theoretical considerations suggest that the oxygen generated by the dissociation of endoperoxides can be in an excited singlet state[125].

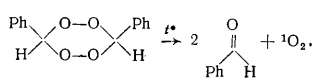
Wasserman and Scheffer[126] showed that the decomposition of 9,10-diphenylanthracene peroxide (I) in the presence of suitable acceptors of singlet oxygen can be used to promote

typical singlet oxygen reactions:



(I)

Similarly, singlet oxygen can be generated[127] by heating 3,6-diphenyl-1,2,4,5-tetroxan (II):



d) Decomposition of the O_2^- ion

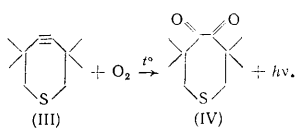
The peroxide ion O_2^- is a potential source of singlet oxygen, since by losing an electron of the appropriate spin it can give either molecular oxygen in the ground state or singlet excited oxygen[14]:

$$^2O_2^- \rightarrow {}^{1,3}O_2 + e^-$$

Evidence of sensitised fluorescence has been detected[128] by adding various fluorescent dyes to a saturated solution of potassium peroxide in dimethylsulphoxide. This was interpreted[128] as evidence for the formation of singlet oxygen in this system, but other chemiluminescence mechanisms cannot be excluded, and doubts were later expressed[129] on this conclusion.

e) Thermal preparation of singlet oxygen

Turro and coworkers[130] reported that the seven-membered alkyne compound 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne (III) when heated (~90 °C) in the dark in the presence of atmospheric oxygen yields the dione (IV) with chemiluminescence [Eqn.(10)]:



(III) (IV) (10)

The same product is obtained by the reaction between the compound (III) and singlet oxygen. Since atmospheric oxygen is triplet, intercombination conversion must be taking place at some stage during reaction (10). The authors conclude[130] that a reactive intermediate (probably an ionic acetylene–oxygen adduct) is formed during the reaction. They suggest that the triple bond in this adduct increases the probability of finding both the electrons from the electron pair of the oxygen molecule on the same oxygen atom, and hence it increases the probability of forming singlet oxygen by the pairing of these electrons.

Free singlet oxygen is generated by the decomposition of the acetylene–oxygen intermediate complex. In this way the starting compound is regenerated, and therefore the process can be classified as a catalytic thermal generation of singlet oxygen from triplet oxygen. This process could be very important in biological systems.

f) Other chemical sources of singlet oxygen

Peroxyacetyl nitrate (PAN), a component of smog, is easily decomposed in the presence of bases[14]:

$$CH_3\overset{O}{\overset{\|}{C}}OONO_2 + 2OH^- \rightarrow CH_3\overset{O}{\overset{\|}{C}}O^- + H_2O + NO_2^- + O_2.$$

Steer and coworkers[131] studied this reaction, and detected a weak radiation at 1270 nm during the decomposition of PAN which they assigned to the $O_2(^1\Delta) \rightarrow O_2(^3\Sigma)$ transition. They ascribed the high reactivity of PAN in chemical and biological systems to its ability to generate singlet oxygen.

Some other compounds also could be of interest for the generation of singlet oxygen. They include the monomeric adducts of oxygen with various transition metals[132–135], and also clathrate oxygen compounds[136]. It has been reported[137] that even in oxyhemoglobin singlet oxygen is formed in the light by a reaction photosensitised by heme:

$$Hem—{}^3O_2 \overset{h\nu}{\rightleftarrows} {}^1Hem^*—{}^3O_2 \rightarrow Hem + {}^1O_2.$$

Although heme does not fluoresce, and hence cannot sensitise the formation of $^1O_2$ in the normal way, its physical proximity to an oxygen atom in the oxyhemoglobin molecule appears to compensate for the short life time of the excited state[137].

3. Electrical Discharge

In this physical method of generating singlet oxygen, discovered by Noxon[138] and developed by various workers[12,111,139,140], an electrodeless microwave or radio-frequency discharge in a stream of oxygen in a discharge tube produces ~10% of $O_2(^1\Delta)$. A mass spectroscopic study of this reaction[142] has shown that the $O_2(^1\Delta)$ continues to exist beyond the discharge region. A small amount of $O_2(^1\Sigma)$ is also produced in the discharge[143], but it rapidly relaxes to $O_2(^1\Delta)$. Oxygen atoms are also formed in the electric discharge, but they can be removed by placing a film of mercuric oxide between the discharge and the observation point[144].

Ozone is another component formed in the discharge. It can react with $O_2(^1\Sigma)$ according to the equation[145]

$$O_2(^1\Sigma) + O_3 \rightarrow O_2 + O_2 + O.$$

The oxygen atoms produced by this reaction can react with a further molecule of ozone:

$$O + O_3 \rightarrow 2O_2.$$

In the absence of ozone and other gases the de-activation of $O_2(^1\Delta)$ and $O_2(^1\Sigma)$ occurs mainly through collisions with the walls of the flow system[140].

4. Incandescent Lamps as Sources of Singlet Oxygen

Khan has shown[146] that electronically excited molecular oxygen can be generated by an ordinary tungsten filament lamp. He found that the radiation from a tungsten filament lamp consists of a series of distinct peaks on a continuous background, and he noted that these peaks correspond to emission bands which had been previously assigned to simultaneous transitions of oxygen pairs. It is assumed that excited oxygen molecules are formed on the tungsten surface, and are then emitted from this surface[147].

Spectroscopic observations[146] have led to the suggestion[14] that the weak luminescence at 520–620 nm which accompanies the chemisorption of oxygen on clean tungsten surfaces[148] may also be due to radiation from excited oxygen molecules.

A relationship between the weak luminescence observed[149] at 600–800 nm during the adsorption of oxygen molecules on various solid oxide surfaces and the formation of singlet oxygen molecules is also possible.

III. METHODS OF DETECTION OF SINGLET OXYGEN

1. Gas-phase Methods

Various methods of detecting singlet oxygen in the gas phase are discussed in recent reviews[1,12,14].

a) Paramagnetic resonance

Oxygen in the $^1\Delta$ state is paramagnetic by virtue of its orbital angular momentum, and several workers[60,119,150–152] have observed and analysed the paramagnetic resonance spectrum of $O_2(^1\Delta)$ in a discharge. In particular, signals corresponding to transitions with $\Delta M = 1$ have been observed for states with a full angular momentum $J = 2$ in addition to the normal signals for the triplet ground state of oxygen. In this way it was shown that the concentration of $O_2(^1\Delta)$ is 10% of the total concentration of oxygen in the discharge. The same method has been used to demonstrate the formation of $O_2(^1\Delta)$ in the gaseous decomposition products of the triphenyl phosphite–ozone adduct[119], and the formation of $O_2(^1\Delta)$ by energy transfer from sensitisers in the triplet state[60,152].

The EPR method is specific for the $^1\Delta$ state of oxygen, because the $^1\Sigma$ state is diamagnetic.

b) Emission spectroscopy

Optical radiation from the $O_2(^1\Delta)$ and $O_2(^1\Sigma)$ molecules can be detected in the gas phase[10,26,27,110,138,139,153–157]. Single molecular transitions occur at 1270 and 760 nm respectively [see Eqn.(9)]. At high oxygen pressures the cooperative (or bimolecular) radiation bands at 634 and 703 nm are easily observed [see Eqn.(3)], as well as the weaker bands at 381 and 478 nm [Eqn.(4)].

An important advantage of the emission spectroscopy method is its ability to detect both $O_2(^1\Sigma)$ and $O_2(^1\Delta)$ over a wide pressure range, whereas by the EPR method $O_2(^1\Delta)$ can be detected only at pressures of several Torr. The sensitivity of the method can be raised still further by using a reflective amplifier to detect the radiation[158].

c) Photo-ionisation

The ionisation potentials of singlet oxygen molecules in $^1\Delta$ and $^1\Sigma$ states are lower (by 1.0 and 1.6 eV respectively) than the ionisation potential of the $^3\Sigma$ ground state (12.5 eV).[159] The photo-ionisation method of detecting excited oxygen is based on this difference[160–163]. The method was used initially with monochromatic excitation[160–162], but later a large increase in sensitivity was obtained by using the resonance lines of the inert gases to ionise excited oxygen molecules[163]. For example, the krypton line at 1165 Å selectively ionises $O_2(^1\Sigma)$, whereas the argon resonance lines at 1067 and 1048 Å ionise both $O_2(^1\Delta)$ and $O_2(^1\Sigma)$, but not $O_2(^3\Sigma)$. The method has yielded valuable information on the rate constants of various reactions of singlet oxygen in the gas phase.

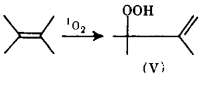
Though the photo-ionisation method is very sensitive, its applications are limited, because the method is not appropriate to systems containing organic molecules, oxides of nitrogen, or other compounds having an ionisation potential lower than 11 eV.

d) Calorimetry

The isothermal calorimetric method of detecting $O_2(^1\Delta)$ depends on the efficient deactivation of this species on a cobalt-coated platinum wire[10,110,111,164]. The heated wire is exposed to the gas stream, and the concentration of excited oxygen molecules can be calculated from the quantity of heat generated by the deactivation process. It has been shown[10,110] that a wire coated with cobalt can deactivate more than 95% of the $O_2(^1\Delta)$ present in the gas stream. The main disadvantage of this method is its lack of selectivity, since $O_2(^1\Sigma)$, atomic oxygen, and any other species in an excited state present in the gas can contribute to the heat evolution.

2. Methods of Detecting Singlet Oxygen in the Condensed Phase. Effect of the Solvent on the Life Time of Singlet Oxygen

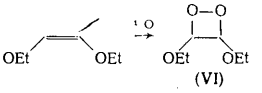
Since the life time of singlet oxygen in the condensed phase is approximately eight orders of magnitude [for $O_2(^1\Delta)$] and ten orders of magnitude [for $O_2(^1\Sigma)$] lower than in the gas phase (see Table 1), most of the methods used to detect singlet oxygen in the gas phase are inappropriate for solutions. Chemical methods are used for solutions, but they are not always reliable. Thus, the reaction of TME with singlet oxygen produces the rearranged allyl hydroperoxide (V):[6,7,30]



(V)

The formation of this hydroperoxide is usually taken as an indication of the presence of $^1O_2$.[85,128] However, there is evidence that this allyl hydroperoxide is formed also when TME reacts with oxygen in the ground state by a chain reaction mechanism including free-radical intermediates[120,165,166].

Singlet oxygen reacts with vinyl diethers to form dioxetanes (VI):[14]



(VI)

However, the same products can be obtained from "non-singlet" oxidation reactions[167], and additional experiments are needed to exclude other possible reactions. These involve adding one or two singlet oxygen fluorescence quenchers (for example, β-carotene, or a tertiary amine such as 1,4-diazobicyclo[2,2,2]octane), and also a typical inhibitor of free-radical auto-oxidation (a substituted phenol). The role of singlet oxygen can be inferred from a comparison of the two experiments.

Of all the reactions examined only the 1,4-cycloaddition to conjugated dienes can be used as an unambiguous test of the presence of singlet oxygen, since no other reagent appears to give the same product[165].

A new method of detecting singlet oxygen in solutions, based on measurements of the life time of singlet oxygen in solutions by infrared spectroscopy, was developed by Merkel

and coworkers[168,169]. These workers found that the life time of singlet oxygen is surprisingly very sensitive to the nature of the solvent. They generated[168,169] singlet oxygen ($\sim 5 \times 10^{-5}$ M) by energy transfer from Methylene Blue triplets excited by light pulses from a ruby laser. The singlet oxygen was then determined spectroscopically by its reaction with the coloured acceptor DPBF to give a colourless product. Measurements of the bleaching rate at two different acceptor concentrations gave the life time of the singlet oxygen and the rate constant of the reaction. When the concentration of DPBF was too low for this reaction to be the main deactivation path of the $O_2(^1\Delta)$ the life time of the singlet oxygen was calculated directly.

Table 3. Solvent dependence of the life time of $O_2(^1\Delta)$.[168,169]

Solvent	Water	Heavy water	Methanol	Ethanol	Cyclohexane	Benzene	Acetone	Chloroform	Hydrogen sulphide	Carbon tetrachloride
Life time of $O_2(^1\Delta)$, μs	2	20	7	12	17	24	26	60	200	700

Table 4. Solvent dependence of the life time of $O_2(^1\Delta)$.[171]

Solvent	n-Butanol	t-Butanol	Benzene methanol (4:1)	Bromobenzene/methanol (4:1)	Pyridine	Dioxan
Life time of $O_2(^1\Delta)$, μs	19±3	34±4	26±5	23±4	33±15	32±10

The results[168,169] revealed no correlation between the life time of the singlet oxygen and properties of the solvent such as the viscosity and dielectric constant. The same conclusion was reached independently in another investigation[170]. Merkel and coworkers[168,169] also found that the life time of singlet oxygen is 10 times higher in D_2O than in ordinary water (see Table 3).

More recently, measurements of life time by flash photolysis have been reported for other solvents (see Table 4).[171]

The deuterium isotope effect has been used[168,169] as a new method of detecting singlet oxygen in solutions. By monitoring the rate of bleaching of DPBF (10^{-5} M) in H_2O/CH_3OH (1:1) and D_2O/CD_3OD (1:1) mixtures under otherwise identical conditions they noted a ten-fold increase in the effectiveness of photo-oxidation in the deuterated solvent. Since the rate constant was unaffected by the deuteration, a ten-fold increase in the life time of singlet oxygen was inferred from these observations.

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Theory of Mixed Isoactive Electrolyte Solutions

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The basic laws of the osmotic theory of mixed isoactive solutions of electrolytes are discussed, and the possibilities of calculating the thermodynamic functions of the mixtures from data for the binary isopiestic solutions are considered. The results obtained for the salting-out effect in extraction systems are presented as an illustration of the theory. 94 references.

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I. INTRODUCTION

The theory of isoactive solutions has been applied increasingly in theoretical work and in practical calculations in recent years. Work during the past 10–15 years has produced the first theory able to deal with both dilute and concentrated (up to saturation) solutions of electrolytes. This theory relies on comparisons of the properties of mixed solutions with those of the initial binary systems at constant activity of the solvent (isopiestic method). Electrolyte solutions have many common features, and it seems logical to use the properties of binary solutions to calculate the corresponding properties of electrolyte mixtures. However, in principle, the general conclusions of the theory can be applied to any system.

The theory can be said to have begun in 1936, when Zdanovskii's rule was published[1] (the fundamental relationship in this theory). However, general interest in Zdanovskii's rule became evident only in the 1960's, stimulated by discussions of its physical significance and of its role in solution thermodynamics. We should note that almost all the theoretical foundations of the theory of isoactive solutions were laid by Soviet scientists.

The general thermodynamic relationships used in the isopiestic method are discussed by Kirgintsev[2]. In this review we shall examine the limiting laws and the possibility of calculating the properties of mixed systems from data for the binary solutions.

II. LAW OF IDEAL MIXING OF ISOPIESTIC SOLUTIONS

The deviation from ideal behaviour of the solvent in a solution is usually characterised by an osmotic coefficient. In our studies of salting-out in electrolyte solutions[3–5] we have pointed out that the osmotic coefficient also describes the tendency of the solute to take up solvent (especially water). This tendency is described particularly well by the molal osmotic coefficient ϕ, defined by the expression

$$\ln a_w = -0.001\ M\nu m\varphi, \qquad (1)$$

where a_w is the activity of the solvent, M is its molecular weight, ν is the stoichiometric coefficient of the electrolyte, and m is the molal concentration of the solute.

Formula (1) is written for a binary solution. If the solution contains several solutes the formula becomes

$$\ln a_w = -0.001 M\varphi_m \sum \nu_i m_i. \qquad (2)$$

The osmotic coefficient of the mixed solution (ϕ_m) is a measure of the average tendency to take up solvent for the particular mixture of solutes. In order to determine the contribution of each component we need to consider the limiting case in which the specific interaction between the components is negligibly small, i.e. we must assume that the molecules or ions of the solute experience the same effect from the other components in the mixed solution as in a binary solution with solvent at the same activity (where the effect arises entirely from like molecules or ions). In such a solution the components have the same tendency to take up solvent as in a binary solution of the same activity, since the solvent has the same "lack of attractiveness" in the two media. The numbers of solvent molecules oriented around a given ion remain the same. Under these conditions the osmotic coefficients of a given component in the binary and in the mixed solution having the same solvent activity should be the same[3].

Thus, for this particular limiting case Eqn.(2) can be written as a sum of the contributions of the individual components to the decrease in the activity of the solvent:

$$\ln a_W = -0.001 M \sum \nu_i m_i \varphi_i^*, \qquad (3)$$

where ϕ_i^* is the osmotic coefficient of the binary solution in isopiestic equilibrium with the mixed solution. (Throughout this reivew we shall use an asterisk to denote parameters referring to isopiestic binary solutions.)

From Eqns.(2) and (3) we obtain

$$\varphi_m = \sum \nu_i m_i \varphi_i^* / \sum \nu_i m_i \text{ or}$$
$$\varphi_m = \sum y_i \varphi_i^*, \qquad (4)$$

where y_i is the ion fraction defined as $\nu_k m_k / \Sigma \nu_i m_i$. Thus ϕ_m is an additive function of composition. Therefore, under these conditions the osmotic pressure generated by a given electrolyte in a mixture is proportional to the ionic concentration of the electrolyte over the whole range of ion fractions. The postulated equality of the osmotic coefficients of the component in isopiestic solutions (i.e. Eqn.(4) has been confirmed[5] from the theoretical and experimental results

of many authors[6-15] for various mixed solutions of alkali metal and other chlorides and nitrates. Experimental results agreed within 1–2% with those calculated from data for the isopiestic binary solutions (with total salt concentrations as high as 3.0–5.0 *m*).

Hence, dividing Eqn.(3) by Eqn.(1) for isopiestic mixed and binary solutions, we obtain[3] the expression known as Zdanovskii's rule:

$$\sum_i m_i/m_i^* = 1, \qquad (5)$$

where m_i^* is the molality of the binary solution having a solvent activity identical to that of the mixed solution. Zdanovskii arrived at this rule purely empirically[1], and at first believed it to be approximate and valid in special cases only. Th law states that when isopiestic binary solutions are mixed the activity of the solvent is unchanged in the absence of specific interactions between the solutes.

Dividing (5) by the total molality or by the total ionic concentration gives, respectively,

$$\frac{1}{m} = \sum_i \frac{1}{m_i^*} x_i \text{ and } \frac{1}{\nu m} = \sum_i \frac{1}{\nu_i m_i^*} y_i, \qquad (6)$$

whence we find that the reciprocal total molality and the reciprocal total ionic concentration are additive functions of composition (x is the mole fraction).

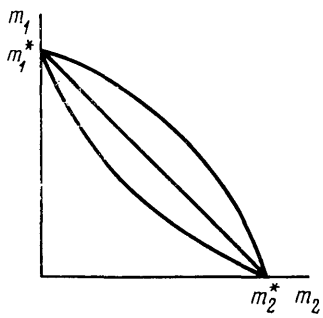


Figure 1. Isotherm–isobars of water in a ternary water–salt system.

For ternary aqueous salt systems with two dissolved electrolytes *1* and *2* Eqns.(5) and (6) take the form

$$m_1/m_1^* + m_2/m_2^* = 1 \qquad (7)$$

and

$$\frac{1}{m} = \frac{1}{m_1^*} x_1 + \frac{1}{m_2^*} x_2. \qquad (8)$$

According to these two equations Zdanovskii's rule can be expressed graphically by straight-line plots (Figs.1 and 2). Its validity has been demonstrated for a large number of systems by Zdanovskii himself and by other workers. Existing experimental information, reported from different laboratories, shows that in mixed solutions of electrolytes with a common anion the deviations from Zdanovskii's rule are usually less than 1–2%. These solutions include the halides, nitrates, and sulphates of the alkali and alkaline-earth metals, and various other salts, at concentrations up to saturation. The fullest bibliography on this topic is given in Ref.16, but it is already seriously out of date.

This discussion of the thermodynamic significance of Zdanovskii's rule allows us to generalise the rule and to conclude that it should apply not only to solutions of salts with a common anion, as had previously been assumed, but also to mixed solutions from any system[3]. This conclusion was confirmed experimentally for solutions with a common cation[3] (including mixtures of strong acids) and for systems without a common ion[17,18]. The latter systems were subsequently studied in detail in our laboratory, following a suggestion by G.I.Mikulin, as quaternary reciprocal systems.

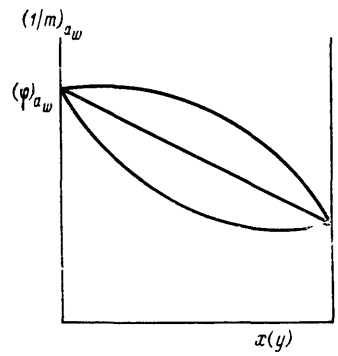


Figure 2. Reciprocal total molality and osmotic coefficient against composition of the ternary solution.

All the available results show that the only condition for the validity of Zdanovskii's rule on mixing binary solutions of electrolytes is the absence of specific interactions between the ions, so that the form of the ions and of their associations is unchanged by the conversion of the binary solution into a mixed solution. Hence no redistribution of the solvent among the components takes place when isopiestic solutions of this type are mixed. For example, large deviations from Zdanovskii's rule are observed[19,20] on mixing solutions of caesium and cobalt chlorides, because the two cations have very different affinities for the chloride ion. On the other hand, isopiestic solutions of cobalt and nickel chlorides can be mixed in exact accordance with Zdanovskii's rule, in spite of the well known chemical interaction between the cations and the anions. This is because of the similarity in properties of the cobalt and nickel ions towards the chloride ion: as a result, there is no redistribution of the chloride ions on mixing, and hence no redistribution of the water.

In the absence of specific interactions between the electrolytes it follows from Eqns.(1)–(3) that the total osmotic activity (as well as the activity of the water) is unchanged when isopiestic solutions are mixed. The total osmotic activity remains equal to the sum of the osmotic activities of the binary solutions, i.e.

$$\sum \nu_i m_i \varphi_i^* = \text{const.} \qquad (9)$$

This expression conveniently characterises the behaviour of solutes on mixing. It is formally similar to the law of constant ionic strength, but it is more strict as well as having greater generality, since it is applicable also to concentrated solutions. If the solutions being mixed have equal (or similar) osmotic coefficients the law of constant osmotic

activity (9) becomes a law of constant ionic concentration, since in this case the isopiestic binary solutions will have identical ionic concentrations and the mixing will affect neither the activity of the water nor the ionic concentration of the resulting mixed solution. This follows from Eqn.(5) for the condition

$$m_1^* = m_2^* = \ldots m_i^*.$$

The direct relationship which we have established between Zdanovskii's rule and the postulate of equal osmotic coefficients of the components in isopiestic solutions, and the resulting additivity of the properties [Eqns.(4) and (6)], suggest that the two laws are identical and are both limiting laws. Additional evidence for this statement comes from the following considerations. Constancy of the solvent activity and of the osmotic activity of the electrolytes on mixing is possible only when the excess Gibbs free energy is zero ($G_m^E i = 0$). Since the activities are related to the chemical potentials, this is a sufficient condition for constancy of the solvent activity, i.e. for the validity of Zdanovskii's rule. However, it follows from the expression

$$G_m^{Ei} = \Delta H - TS_m^{Ei} = \Delta H + T\partial G^{Ei}/\partial T,$$

(where ΔH is the enthalpy of mixing, T is the temperature, and $S_m^E i$ is the excess entropy of mixing) that, in general, we have $\Delta H = 0$ for $G_m^E i = 0$, i.e. that mixing is ideal when Zdanovskii's rule applies. Nevertheless non-ideal mixing with $G_m^E i = 0$ is possible in some cases: this occurs when a small enthalpy change can be compensated (at a given temperature) by the excess entropy term.

Thus, in general mixed solutions free from specific interactions between the dissolved components can be prepared by ideal mixing of binary solutions of the components in isopiestic equilibrium. We have proposed the term isoactive for solutions of this type[18,21].

The first evidence of the ideality of mixing in accordance with Zdanovskii's rule was obtained by Vdovenko and Ryazanov[22,23], who also formulated the analogy between Zdanovskii's rule and Raoult's law. A similar demonstration was later given by Kirgintsev[2] by introducing a new thermodynamic function (the aqueosity of the solution).

It follows that Zdanovskii's rule can no longer be treated as partial and approximate: it is a limiting expression, or, more strictly, a limiting law[24]. Hence, experimental results on mixed solutions cannot be classified as confirming (or not confirming) the generality of this law. Zdanovskii's law is entirely general, and it can be used as a standard of comparison for the properties of real solutions: in other words, the whole of the experimental information can be interpreted from the standpoint of deviations from this law. This is the essential feature common to all limiting laws. No "correction" to Eqn.(5) can increase its generality, since it introduces some indeterminacy arising from the need to determine the correction experimentally for each specific system.

III. ADDITIVITY OF THE PROPERTIES OF MIXED SOLUTIONS OF ELECTROLYTES

The ideal mixing of isopiestic binary solutions of electrolytes allows us to calculate all the thermodynamic properties of mixed isoactive solutions from the properties of the initial binaries. The difference from the calculation of the properties of ideal solutions is that the mixing of individual components is replaced (in the case of isoactive solutions) by the mixing of the appropriate binary solutions in isopiestic equilibrium with the mixed isoactive solution. Thus all the calculations begin with a determination of the so-called isopiestic concentrations m_i^* of the binary solutions, usually by a selection method relying on successive approximations[1]. The concentration dependence of the activity of the water in the binary solutions is first established from tabulated data (Fig.3). A suitable value of the activity of water is then chosen, and the corresponding concentration is inserted into Eqn.(5) (the concentrations of the components in the mixed solution m_i are assumed to be known). If the sum differs from unity the operation is repeated: when the results are satisfactorily consistent the calculated concentrations of the binary solutions will be isopiestic.

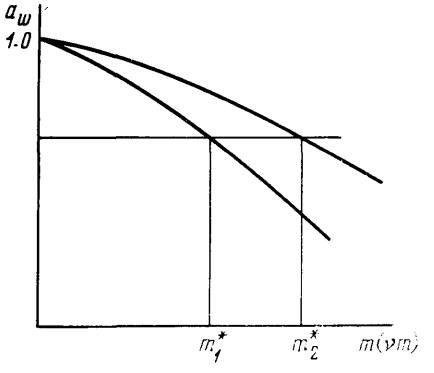


Figure 3. Determination of the isopiestic concentrations m_1^* and m_2^* for a ternary solution.

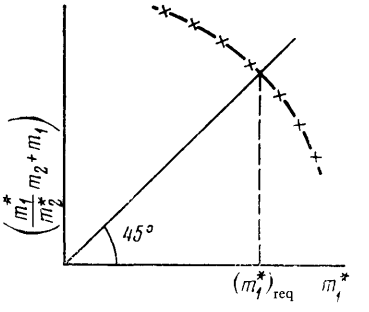


Figure 4. Graphical determination of the required value of m_1^*.

The need for selection can be avoided by using the method proposed in Ref.22. Zdanovskii's law for a ternary solution is written

$$\frac{m_1^*}{m_2^*} m_2 + m_1 = m_1^*.$$

The ratio m_1^*/m_2^* can be taken from tabulations, or alternatively we can use Fig.3 and draw a number of sections for different water activities. We then plot (Fig.4) the function $(m_1^*/m_2^*)m_2 + m_1$ against the corresponding value of m_1^*. The intersection of the resulting curve with a straight line drawn

through the origin at 45° gives the wanted value of m_1^*. The concentration m_2^* is found in a similar way. In extensive calculations it is convenient to establish the approximate $a_W = f(m_i)$ expressions and to solve them simultaneously with Eqn.(5) on a computer[25].

These methods can be used only when the isopiestic concentrations do not exceed the solubility limits of the components. If the isopiestic concentration is higher than the solubility it cannot be determined experimentally. Zdanovskii overcame this problem by graphically extrapolating the $a_W = f(m^*)$ relationships to the supersaturated solution region. In our work[25] the same result was achieved by using analytical expressions as approximations to the experimental data. If experimental values of the activity of water are available for solutions saturated with the first electrolyte, i.e. for point C lying on the m_1^S–m_{12}^S curve of Fig.5, the calculation is possible[26]. If the coordinates of this point are m_1 and m_2 we can solve Eqn.(5) for m_1^* and obtain

$$m_1^* = m_1 m_2^* / (m_2^* - m_2).$$

Therefore the quantity m_1^*, corresponding to a given activity of water, can be found if m_1, m_2, and m_2^* are known. Mikulin[27] carried out calculations of this type in his graphical–analytical treatment of data for the KCl–NaCl–H_2O, KNO_3–$NaNO_3$–H_2O, and NaCl–$CaCl_2$–H_2O systems.

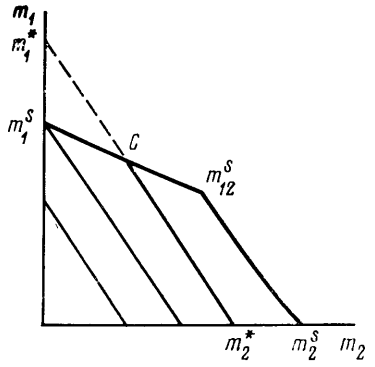


Figure 5. Determination of the isopiestic concentration beyond the solubility limit.

If the isopiestic concentrations of the binary solutions and their properties are known, the corresponding property for the multi-component isopiestic solution is easily calculated. Ideality of mixing is equivalent to zero changes in enthalpy and in volume on mixing: it follows that these properties (and others, related to them) are additive. In mixed isoactive solutions additivity is expected in relation to the isopiestic binary solutions. For example, in order to form a ternary solution of given composition the initial binary solutions have to be mixed in the appropriate proportions. According to Zdanovskii's law (5), in order to prepare a mixture of electrolytes having a common ion in which the concentration of the first electrolyte is m_1 and that of the second electrolyte is m_2 we have to mix m_1/m_1^* parts of the binary solution of electrolyte *1* and m_2/m_2^* parts of the binary solution of electrolyte *2*. The enthalpy of the resulting ternary solution will be[23]

$$H = \frac{m_1}{m_1^*} H_1^* + \frac{m_2}{m_2^*} H_2^* \quad \text{or} \quad H = \sum_i \frac{m_i}{m_i^*} H_i^*. \tag{10}$$

In a similar way we can obtain an expression for the volume:

$$V = \frac{m_1}{m_1^*} V_1^* + \frac{m_2}{m_2^*} V_2^* \quad \text{or} \quad V = \sum_i \frac{m_i}{m_i^*} V_i^*. \tag{11}$$

The additivity of the enthalpy and volume allows us to calculate other properties of the multicomponent solutions derived from these functions. For example, Zdanovskii[28] obtained a similar expression for the specific heat

$$C = \frac{m_1}{m_1^*} C_1^* + \frac{m_2}{m_2^*} C_2^* \quad \text{or} \quad C = \sum_i \frac{m_i}{m_i^*} C_i^* \tag{12}$$

and for the density (the reciprocal of the specific volume)

$$\frac{1}{\rho} = \frac{m_1}{m_1^*} \frac{1}{\rho_1^*} + \frac{m_2}{m_2^*} \frac{1}{\rho_2^*} \quad \text{or} \quad \frac{1}{\rho} = \sum_i \frac{m_i}{m_i^*} \frac{1}{\rho_i^*}. \tag{13}$$

The entropy is defined by the equation

$$S = \frac{m_1}{m_1^*} S_1^* + \frac{m_2}{m_2^*} S_2^* + \Delta S_m \quad \text{or} \quad S = \sum_i \frac{m_i}{m_i^*} S_i^* + \Delta S_m, \tag{14}$$

where ΔS_m is the ideal entropy of mixing. The equation for the Gibbs free energy therefore becomes

$$G = \frac{m_1}{m_1^*} G_1^* + \frac{m_2}{m_2^*} G_2^* + \Delta G_m \quad \text{or} \quad G = \sum_i \frac{m_i}{m_i^*} G_i^* + \Delta G_m, \tag{15}$$

where ΔG_m is a purely entropic term. When the ideality of the mixing of isopiestic solutions has been established Eqns.(10)–(15) can be used in the simplified form shown.

The equation for the change in entropy during ideal mixing of isopiestic binary solutions was obtained by Vdovenko and Ryazov by a statistical method[23]:

$$\Delta G_m = -T\Delta S_m = RT\left(\nu_1 m_1 \ln \frac{\nu_1 m_1}{\nu_1 m_1 + \nu_2 m_2} + \nu_2 m_2 \ln \frac{\nu_2 m_2}{\nu_1 m_1 + \nu_2 m_2} - \right.$$
$$\left. - \nu_{-1} m_1 \ln \frac{\nu_{-1} m_1}{\nu_{-1} m_1 + \nu_{-2} m_2} - \nu_{-2} m_2 \ln \frac{\nu_{-2} m_2}{\nu_{-1} m_1 + \nu_{-2} m_2}\right), \tag{16}$$

where the subscripts −1 and −2 denote the anions of the first and the second electrolyte. If the electrolytes *1* and *2* have no common ion the last two terms drop out of the equation.

All these expressions for thermodynamic properties per mole of solute can be written in the form[29]

$$\Phi^m = x_1 \Phi_1^{m*} + x_2 \Phi_2^{m*} + \Delta\Phi_{m.id.}^m, \tag{17}$$

where Φ_i^m are the thermodynamic functions referred to one mole of solute, and $\Phi_{m.id.}^m$ is the change in the thermodynamic functions caused by ideal mixing of the isopiestic solutions.

If the binary solutions being mixed have the same (or similar) concentration dependences of the water activity, or similar values of the osmotic coefficients under isopiestic conditions, the total ionic concentration in the mixed solution will be equal (or similar) to the ionic isopiestic concentrations in the binary solutions [see Eqns.(1) and (3)]. In this case all the equations for additive functions (Φ) again take a form similar to Eqn.(17):

$$\Phi = x_1 \Phi_1^* + x_2 \Phi_2^* + \Delta\Phi_{m.id.} \quad \text{or} \quad \Phi = \sum_i x_i \Phi_i^* + \Delta\Phi_{m.id.}. \tag{18}$$

The properties of one binary solution may have to be inferred from those of the mixed solution and of the other binary solution. For example, it is difficult (or even impossible) to determine the properties of solutions of salts undergoing hydrolysis. Hydrolysis can be suppressed by adding acid to the solution: if the mixture can be assumed to be an isoactive solution the properties of the binary solution of hydrolysable electrolyte in a hypothetical non-hydrolysed acid-free form[30] can easily be calculated by the above formulae.

The properties of isoactive systems are directly related not only to those of the isopiestic binary solutions but also to those of solutions of any concentration. This is because

when solutions with different solvent activities are mixed only redistribution of the solvent takes place between the electrolytes. "Internal" levelling of the activity occurs, increasing concentration of one component being accompanied by increase ing dilution of another. The process taking place within the solution can be described as a succession of steps: 1) dilution and concentration of the binary solutions to the isopiestic concentration levels, and 2) ideal mixing of the isopiestic binary solutions. Thus, any property of the solution can be expressed as the sum

$$\Phi_i = \Phi_i^* + \Delta\Phi_{m_i - m_i^*} \quad \text{or} \quad \Phi_i^* = \Phi_i - \Delta\Phi_{m_i - m_i^*}, \tag{19}$$

where $\Delta\Phi_{m_i^I - m_i^*}$ is the change in the function for the binary solution upon conversion from the concentration chosen for mixing to the isopiestic concentration.

It has been shown[29] that the thermodynamic functions of mixing can be calculated by expressions similar to (10)–(17):

$$\Delta\Phi_m = \frac{m_1}{m_1^*}\Delta\Phi_{m_1' - m_1^*} + \frac{m_2}{m_2^*}\Delta\Phi_{m_2' - m_2^*} + \Delta\Phi_{m.id.} \tag{20}$$

If the thermodynamic functions are calculated for one mole of electrolyte we have

$$\Delta\Phi_m^m = x_1\Delta\Phi_{m_1' - m_1^*}^m + x_2\Delta\Phi_{m_2' - m_2^*}^m + \ldots + \Delta\Phi_{m.id.}^m \tag{21}$$

Since the mixing effects during formation of isoactive solutions are determined by the solvent redistribution and by the ideal entropy changes which follow the mixing of isopiestic solutions, an appropriate term is added to Eqns.(20) and (21): in the case of functions independent of the entropy of mixing this term is zero. For example, for the enthalpy of mixing we have

$$\Delta H_m^m = x_1\Delta H_{m_1' - m_1^*}^m + x_2\Delta H_{m_2' - m_2^*}^m. \tag{22}$$

This expression was obtained by Zdanovskii and Deryabina[31] for the enthalpy change caused by the redistribution of the solvent. It is evident from Eqn.(19) that the expression for a generalised property of the mixed solution in terms of the properties of binary solutions of arbitrary concentration takes the form of Eqns.(10)–(17):

$$\Phi = \frac{m_1}{m_1^*}(\Phi_1 - \Delta\Phi_{m_1' - m_1^*}) + \frac{m_2}{m_2^*}(\Phi_2 - \Delta\Phi_{m_2' - m_2^*}) + \ldots + \Delta\Phi_{m.id.} \tag{23}$$

If the property is calculated for one mole of the electrolyte the expression becomes

$$\Phi^m = x_1(\Phi_1^m - \Delta\Phi_{m_1' - m_1^*}^m) + x_2(\Phi_2^m - \Delta\Phi_{m_2' - m_2^*}^m) + \ldots + \Delta\Phi_{m.id.}^m \tag{24}$$

Thus, if no specific interactions between the electrolytes are found in the mixed solution (as compared with the binary solutions) the properties of the mixed solution—including the functions of mixing of the binary solutions—can be calculated from the properties of the latter without further experiments.

To conclude this Section we should stress that in principle any mixed solution of electrolytes, even one in which chemical interactions are present, can be treated as isoactive if the compositions of the resulting complexes are known. The analogy with ideal associated solutions[32] is appropriate. By allowing for the chemical interaction we can compare these systems with the binary isopiestic solutions of their components. However, calculation of the thermodynamic properties of the system is possible only if the necessary data for the binary solutions of the initial components and of the resulting components are available. If complexes are formed our formulae will have limited value, since very few data are available on the properties of complex solutions (especially when the stability of the complexes is low). However, this approach offers the possibility of calculating complex formation in solutions[33].

All the arguments presented here follow from the postulate that isoactive solutions can be treated as "an ideal mixture of binary solution quasi-particles"[34]. The quasi-particles can be simple ions, complex ions, or neutral molecules, i.e. any formation known to be present in real solutions. Deviations from the limiting law are a result of the impossibility of allowing for the large number of states in which the dissolved components may exist. If allowance can be made even only for the fundamental states the mixed solutions can be "reduced" to isoactive or almost isoactive solutions. This is clearly shown by our work[35–37] on systems containing sulphuric acid, which has only a weak second dissociation though most of the thermodynamic properties of its solutions have been determined with respect to full dissociation. By ignoring the second dissociation step and treating sulphuric acid as a 1–1 electrolyte we were able to show experimentally[36,37] that mixtures of sulphuric acid and monobasic inorganic acids (nitric, perchloric, hydrochloric) or lithium or potassium hydrogen sulphates can be treated as isoactive with acceptable precision (up to ±3%). In practice, mixtures of lithium sulphate and hydrogen sulphate are also isoactive: the deviations increase with the size of the alkali metal cation. All the thermodynamic parameters of the mixed solutions mentioned above were calculated in our laboratory[37] by using this effect.

IV. ACTIVITY COEFFICIENTS OF ELECTROLYTES IN MIXED ISOACTIVE SOLUTIONS

The condition for the formation of an isoactive mixed solution from isopiestic binary solutions is ideal mixing ($\Delta G_m^E i = 0$). From this condition we can easily obtain an expression for the activity coefficients (γ) of the components in the mixed solution, which vary only as a result of changes in the overall ionic concentration. This involves comparing the chemical potentials, measured from the corresponding standard states[24]:

$$\nu_1 RT \ln a_1 = \nu_1 RT \ln a_1^* + \nu_1 RT \ln \frac{\nu_1 m_1}{\nu_1 m_1 + \nu_2 m_2}.$$

It follows that

$$\gamma_1 = \nu_1 m_1^* \gamma_1^* / (\nu_1 m_1 + \nu_2 m_2) \quad \text{or} \quad \gamma_k = \nu_k m_k^* \gamma_k^* / \sum \nu_i m_i, \tag{25}$$

Eqn.(25) is known as Mikulin's equation.

A formula of this type for 1–1 electrolytes was first proposed[38] as an approximation, obtained from McCay and Perring's[39] general differential equation. Mikulin[40] and, later, Vdovenko and Ryazanov[22], derived Eqn.(25) for mixtures of electrolytes of different valency types by an exact simultaneous solution of McCay and Perring's equations and Zdanovskii's law (5). Mikulin's equation, like Zdanovskii's law, applies with adequate precision to a very large number of different mixed solutions of electrolytes, including solutions at very high concentrations.

In order to formulate the dependence of the activity coefficient of the electrolyte on the composition at constant water activity we shall express Eqn.(25) in terms of the osmotic coefficients, using Eqns.(1), (2), and (4). We obtain[4]

$$\gamma_1/\gamma_1^* = \varphi_m/\varphi_1^* \tag{26}$$

and for a ternary solution

$$\gamma_1/\gamma_1^* = (1 - \varphi_2^*/\varphi_1^*)\, y_1 + \varphi_2^*/\varphi_1^*, \tag{27}$$

$$\frac{\gamma_1}{\gamma_1^*} = 1 - (1 - \varphi_2^*/\varphi_1^*)\, y_2, \qquad (28)$$

or in terms of the isopiestic concentrations

$$\gamma_1/\gamma_1^* = 1 - (1 - \nu_1 m_1^*/\nu_2 m_2^*)\, y_2. \qquad (29)$$

It follows from (26)–(29) that at constant water activity the activity coefficient of the electrolyte is directly proportional to both its own ion fraction and the ion fraction of the second electrolyte. The slope of the straight-line dependence is determined by the difference (or ratio) of the osmotic coefficients of the binary isopiestic solutions (or of the isopiestic concentrations). Eqns.(27)–(29) are reminiscent of Harned's rule[41], though they differ from it in having a thermodynamic foundation and hence in being applicable without exception to all isoactive solutions, i.e. to solutions in which specific interactions between the electrolytes can be neglected.

In order to convert Eqns.(28) and (29) into a form similar to Harned's rule we shall take logarithms [of Eqn.(28), say]. Series expansion of the logarithm on the right-hand side, truncated after the first term, gives

$$\ln \gamma_1 = \ln \gamma_1^* - (1 - \varphi_2^*/\varphi_1^*)\, y_2. \qquad (30)$$

From these considerations we may conclude that a linear dependence of the activity coefficient on composition is characteristic, strictly speaking, of the condition of constant solvent activity (or constancy of osmotic activity), and not constancy of the ionic strength (as required by Harned's rule). We should note that at the water activity corresponding to the intersection of the $a_w = f_1(m_1)$ and $a_w = f_2(m_2)$ plots the coefficient of y_2 is zero, and on either side of this point the coefficient has different signs.

If the osmotic coefficients in the isopiestic solutions of electrolytes being mixed are equal Mikulin's equation for the activity coefficient of one of the components becomes[3]

$$\gamma_k = \gamma_k^* = \text{const}. \qquad (31)$$

This expression follows also from Eqn.(26).

Since the condition of constant water activity in this case, is analogous to constancy of the overall ionic concentration (3), we can infer the following from Eqn.(31): if the electrolytes have equal osmotic coefficients (i.e. equal tendencies for taking up water) their activity coefficients at constant total ionic concentration will be constant (i.e. independent of the component ratio) and equal to the activity coefficient of the component in the binary solution. Eqn.(31) applies strictly, even to concentrated solutions, in the absence of specific interactions between the electrolytes (i.e. for ideal mixing of binary isopiestic solutions of electrolytes). However, the condition of equal osmotic coefficients in the binary solutions is most easily satisfied at low concentrations. We have obtained satisfactory results[3] at total molalities up to 1.5–2.0 for the following systems (which have also been studied by other workers): HNO_3–$CaCl_2$–H_2O, HNO_3–$MgCl_2$–H_2O, HCl–$CaCl_2$–H_2O, HCl–$SrCl_2$–H_2O, HCl–$MgCl_2$–H_2O, HCl–$HClO_4$–H_2O, etc.

The expression (31) is analogous to the ionic strength rule, and yet it reveals the shortcomings of that rule and the advantages of using ionic and osmotic concentrations. The ionic strength rule was confirmed by the Debye–Hückel law, and in some of the contemporary publications[42–44] the law was also compared with Zdanovskii's rule, which had previously been thought to be only an approximation. It was shown[45] that only a special case of Zdanovskii's law, corresponding to equal osmotic coefficients of the components [as in Eqn.(31)], could be compared with the Debye–Hückel law. The Debye–Hückel limiting law describes the ideal mixing of electrolyte solutions to a good approximation only at very high dilutions. The Zdanovskii limiting law also is applicable only to systems without specific interaction between the electrolytes, but its validity is unaffected by the tendency of the electrolytes to take up solvent or by the concentration of the electrolyte.

It is often necessary, especially in radioactive tracer work under industrial conditions, to calculate the thermodynamic activity of a microcomponent in the presence of a macro-component: for example, in the salting-out of micro-components during extraction and adsorption. The application of Eqn.(25) to a micro-component is greatly simplified if the concentration of the micro-component can be ignored in comparison to that of the macro-component. Under those conditions we assume that the total ionic concentration in the denominator of the right-hand side of Eqn.(25) and the isopiestic concentration of the binary solution of the macro-component are equal to the concentration of the macro-component in the mixed solution. Thus, the isopiestic concentration of the micro-component *1* (m_{01}) is determined by the initial concentration of the macro-component *2*, and Eqn.(25) becomes[4]

$$\gamma_{01} = \nu_{01} m_{01}^* \gamma_{01}^* / \nu_2 m_2. \qquad (32)$$

If in one solution substance *1* is the micro-component and substance *2* is the macro-component, and in another solution the roles are reversed, then for equal ionic concentrations of the macro-components the ratio of the activity coefficients of the micro-components in these solutions will be

$$\gamma_{01}/\gamma_{02} = \nu_{01} m_{01}^* \gamma_{01}^* / \nu_{02} m_{02}^* \gamma_{02}^*. \qquad (33)$$

Robinson and Stokes, when discussing mixed solutions of hydrochloric acid and sodium chloride, quote the following "paradoxical result: the activity coefficient of hydrochloric acid in a solution containing effectively only sodium chloride is practically equal to the activity coefficient of sodium chloride in a solution containing effectively only hydrochloric acid"[46]. The explanation of this paradox follows from Eqn.(33). The activity coefficients of the micro-components in these solutions will be similar if the products $\nu m^* \gamma^*$ have similar values. In the case of hydrochloric acid and sodium chloride solutions the ratio of these products is close to unity over a wide range of concentration.

V. THERMODYNAMIC PROPERTIES OF QUATERNARY RECIPROCAL SYSTEMS

It is obvious, from the formulation of the ideal mixing of electrolyte solutions given by Zdanovskii (see Section I), that both the probability and the magnitude of deviations from ideality will be greater if the electrolytes being mixed do not have a common ion. This is mainly the result of ion-exchange interaction in systems without a common ion. Furthermore, in systems which include a like ion the deviations cannot be calculated in terms of the properties of the binary solutions, because the transfer of the ions from one electrolyte to another is accompanied by the formation of complexes which cannot exist in the binary solutions. In systems without common ions the main interaction is ion exchange between the dissolved electrolytes, which can be described by treating the mixture of electrolytes as a system of four reciprocal binary isopiestic solutions, as suggested by Mikulin and Voznesenskaya[47].

Equilibrium in a quaternary reciprocal system is treated as an ionic exchange double decomposition reaction:

$$\underset{1}{AM} + \underset{4}{BN} \rightleftarrows \underset{2}{AN} + \underset{3}{BM}, \qquad (34)$$

Following Mikulin and Voznesenskaya[47], we shall represent a mixed solution of two electrolytes without a common ion in a composition square (Fig.6) relating the concentrations of

the components of the quaternary reciprocal system (34). We shall denote the concentrations of A, B, M, and N by n_A, n_B, n_M, and n_N respectively, and we shall take the total concentrations of electrolytes in the system to be n g-equiv per 1000 g of water. The following relationships will be used for the ion fractions in the case of electrolytes of different valency:

$$x=n_A/n;\ 1-x=n_B/n;\ y=n_M/n;\ 1-y=n_N/n.$$

The concentrations of the electrolytes AM, AN, BM, BN (point S of Fig.6) will be related by the expressions

$$n_1nxy;\ n_2=nx(1-y);\ n_3=n(1-x)y;\ n_4=(1-x)(1-y). \qquad (35)$$

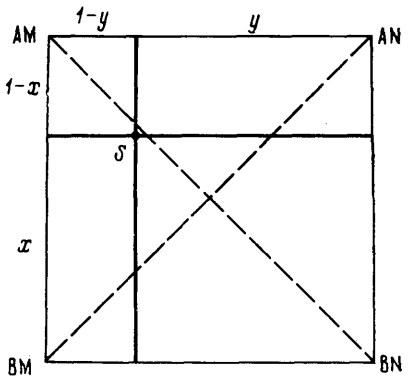


Figure 6. Relationship between the composition of the components in a quaternary reciprocal system (composition square).

We shall also use[48] the expression (4) relating the osmotic coefficient of the mixed solution (ϕ) to the osmotic coefficients in the binary solutions of the electrolytes (ϕ_i^*) at the same water activity. For a quaternary reciprocal system, allowing for the equality

$$\nu_i m_i = \frac{z_i^+ + z_i^-}{z_i^+ z_i^-} n_i = K_i n_i$$

Eqn.(4) becomes

$$\varphi = \sum_i \varphi_i^* K_i n_i \Big/ \sum K_i n_i. \qquad (36)$$

Inserting into this equation the expressions for the concentrations of the electrolytes [Eqn.(35)] we arrive at a formula for the osmotic coefficients of quaternary aqueous reciprocal systems:

$$(\varphi)_{a_w} = \lambda_1\varphi_1^* + \lambda_2\varphi_2^* + \lambda_3\varphi_3^* + \lambda_4\varphi_4^*, \qquad (37)$$

where ϕ_i^* are the osmotic coefficients of the binary isopiestic electrolyte solutions which constitute the quaternary reciprocal system (34). The coefficient λ_i (for example, in the case of electrolyte 1) is given by

$$\lambda_1 = xyK_1/[xyK_1 + x(1-y)K_2 + (1-x)yK_3 + (1-x)(1-y)K_4].$$

Eqn.(37) is valid if no chemical interactions other than ion exchange are present in the solution. It is the analogue of Eqn.(4), obtained by postulating equal osmotic coefficients of the components in the isopiestic solutions. It follows that systems of this type can be treated as quaternary reciprocal systems to which Zdanovskii's law applies. Hence, all the equations given in Section II are fully applicable to mixed solutions of electrolytes without a common ion, for example

$$\Delta H = \frac{m_1}{m_1^*}\Delta H_1^* + \frac{m_2}{m_2^*}\Delta H_2^* + \frac{m_3}{m_3^*}\Delta H_3^* + \frac{m_4}{m_4^*}\Delta H_4^*$$

etc.

On the other hand, if we start from the concentrations of two solutions of electrolytes (without common ions) being mixed, the properties of the mixture are parabolically dependent on the relative amount of one of the components. That this should not be interpreted as a deviation from Zdanovskii's law is evident from the work of Mikulin[47], though he himself states[34] that "Zdanovskii's rule applies only to mixed solutions with a common ion, but it follows from this rule that in quaternary aqueous reciprocal systems the equal water activity plots are in general parabolic". Evidently, Mikulin erroneously identifies Zdanovskii's rule not with Eqn.(5), but with the linearity of the water isotherm–isobar for two components, or with the textual formulation of the law in terms of the mixing of two binary solutions.

In order to calculate the thermodynamic functions directly we must start from the concentrations (in the mixture) of the (two) mixed electrolytes, since the concentrations of the four electrolytes in the equilibrium mixture are unknown. In order to simplify the mathematics we shall assume that the ions from all the electrolytes in the system (34) have identical charges (in absolute value): for example, that the electrolytes being mixed are both 1–1, or 2–2. Under these conditions the following equality applies to the AM(1)–BN(4)–H_2O system:

$$x=y=n_1/(n_1+n_2),$$

and Eqn.(4) becomes

$$(\varphi)_{a_w} = (\varphi_1^* + \varphi_4^* - \varphi_2^* - \varphi_3^*)x^2 + (\varphi_2^* + \varphi_3^* - 2\varphi_4^*)x + \varphi_4^* \qquad (38)$$

or

$$(\varphi)_{a_w} = Ax^2 + Bx + C. \qquad (39)$$

A similar expression was obtained earlier[47] for the reciprocal total molality.

The coefficients A, B, and C can easily be determined from the tabulated values of the corresponding osmotic coefficients of the binary solutions. In this way all the thermodynamic functions of the mixed isoactive solution formed from two solutions of electrolytes without common ions can be calculated. For example,

$$\Delta G = A'x^2 + B'x + C' + \Delta G_M^{id}, \qquad (40)$$

where

$$A' = \Delta G_1^* + \Delta G_4^* - \Delta G_2^* - \Delta G_3^*,$$
$$B' = \Delta G_2^* + \Delta G_3^* - 2\Delta G_4^*,$$
$$C' = \Delta G_4^*.$$

Satisfactory agreement between calculation and experiment is obtained for practically all the systems composed of halides and nitrates of alkali and alkaline-earth metals[17,18,49–51].

Formulae for the activity coefficients of the electrolytes (without common ions) in a mixed solution can be obtained from Eqn.(39). In our calculation[48,52] the McCay–Perring equation[39] was first converted into a form consistent with that of the expression for the osmotic coefficients:

$$\ln\frac{(\nu_1 m_1 + \nu_2 m_2)\gamma_1}{\nu_1 m_1^* \gamma_1^*} = \int_0^{\ln a_w} \left[(1-y_1)\left(\frac{\partial\varphi}{\partial y_1}\right)_{a_w} + \varphi + \varphi_1^*\right]\frac{d\ln a_w}{\ln a_w}. \qquad (41)$$

Simultaneous solution of Eqns.(39) and (41) for electrolytes with the above limitations on the stoichiometric coefficients gave

$$\ln\gamma_1 = \ln\frac{m_1^*\gamma_1^*}{m_1+m_4} - (1-x)^2\int\frac{A}{\ln a_w}\,\mathrm{d}\ln a_w.$$

From the Gibbs–Duhem equation for a binary solution we have

$$\int\frac{\varphi_i^*}{\ln a_w}\,\mathrm{d}\ln a_w = \ln a_i^*,$$

whence

$$\ln\gamma_1 = \ln\frac{m_1^*\gamma_1^*}{m_1+m_4} - (1-x_1)^2\ln\frac{a_1^*a_4^*}{a_2^*a_3^*}. \qquad (42)$$

This formula was first obtained[47] by an entirely different approach. In the case of electrolytes of any valency type the McCay and Perring equation must be solved by using the more complex expression (37).

If the coefficient of x^2 in equations of the type of (39) is zero (i.e. $A=0$) it follows that the quaternary system is not only isoactive but also additive with respect to the separate ions: for example, for the system

$$AX_2+2BY=AY_2+2BX$$

we expect to find

$$\varphi_{AX_2}^* + 2\varphi_{BY}^* = \varphi_{AY_2}^* + 2\varphi_{BX}^*. \qquad (43)$$

In this case the affinities of the two cations for the two anions (or of the two anions for the two cations) are the same. Eqn.(43) applies, for example, to the $CaBr_2$–LiCl–H_2O and $CaCl_2$–KBr–H_2O systems[53].

VI. CALCULATION OF THE OSMOTIC COEFFICIENTS AND ACTIVITY COEFFICIENTS OF SEPARATE IONS

The success of our postulate of equal osmotic coefficients for a component in mixed solutions having the same water activity (in the absence of chemical interactions) suggested the possibility of applying the same approach to separate ions. An analogy was formulated[54] between mixed solutions of electrolytes and binary solutions, which were described as mixed by treating the ions as separate components. In keeping with Eqn.(1), which features the mean ionic molal osmotic coefficient, we can introduce the concept of an osmotic coefficient of the ion and replace Eqn.(1) by an expression for the activity of the solvent in the following terms:

$$\ln a_w = -0.001Mm(\nu_+\varphi_+ + \nu_-\varphi_-). \qquad (44)$$

where ν_+ and ν_- are the stoichiometric coefficients of the ions, and ϕ_+ and ϕ_- are the osmotic coefficients of the ions. Like the osmotic coefficients of the components, those of the ions are a measure of the ability of the given species to take up water. Extending the analogy, we assumed that the osmotic coefficients of a given ion in different solutions must be equal if the activity of water in the solutions is the same and if there is no difference between the ionic interactions (in particular, the chemical interactions) in the different solutions. By adopting these hypotheses and taking an arbitrary electrolyte as standard we can easily calculate the osmotic coefficients of the ions in other solutions.

The standard electrolyte is usually chosen so that $\phi_+^0 = \phi_-^0 = \phi_\pm^0$, and therefore it is usually a 1–1 electrolyte. By comparing Eqn.(44) for a solution of the standard electrolyte with the same equation for the unknown binary solution, having an ion in common with the standard, we obtain expressions for the counter-ion in the unknown solution

$$\nu_{+2}\varphi_{+2} = \nu_{\pm 2}\varphi_{\pm 2} - \nu_-\varphi_\pm^0 \quad\text{and}\quad \nu_{-2}\varphi_{-2} = \nu_{\pm 2}\varphi_{\pm 2} - \nu_+\varphi_\pm^0 \qquad (45)$$

and for the 1–1 electrolytes

$$\varphi_{+2} = 2\varphi_{\pm 2} - \varphi_\pm^0 \quad\text{and}\quad \varphi_{-2} = 2\varphi_{\pm 2} - \varphi_\pm^0.$$

For electrolyte solutions not having an ion in common with the standard we use the scheme KCl → CsCl → CsBr.

Using a solution of potassium chloride as standard we have calculated[54] from the above expressions the osmotic coefficients of the ions in binary solutions of various alkali metal halides at concentrations between 1.0 and 2.0 *m*. As a test of the method, we also calculated the mean ionic osmotic coefficients of electrolytes not having an ion in common with the standard, using the scheme KCl → CsCl → CsBr and KCl → KBr → CsBr. The arithmetic means were compared with tabulations[46]: the deviations were found to be within 2%, confirming the correctness of our assumption of equal osmotic coefficients for ions in isopiestic solutions of these electrolytes.

These favourable results justified an attempt to calculate the activity coefficients of individual ions by Mikulin's equation. If two ternary solutions have one electrolyte in common and equal water activities the ratio of the activity coefficients of the electrolytes in the solutions is

$$\gamma_1/\gamma_1' = (\nu_1'm_1' + \nu_3'm_3')/(\nu_1m_1 + \nu_2m_2).$$

In the standard electrolyte solution $\gamma_{+0} = \gamma_{-0} = \gamma_{\pm 0}$, and therefore the expression for the ions (comparing two binary electrolyte solutions with a common ion) becomes

$$\gamma_+/\gamma_{\pm 0} = 2m_0^*/\nu m^* \quad\text{and}\quad \gamma_-/\gamma_{\pm 0} = 2m_0^*/\nu m^*, \qquad (46)$$

i.e. the ratio of the activity coefficients of the ions in the two solutions having identical water activities is equal to the reciprocal of the ratio of the ionic concentrations of these solutions.

Eqns.(46) are easily generalised for multicomponent solutions:

$$\frac{\gamma_{+m}}{\gamma_{+2}} = \frac{\nu_2m_2^*}{\sum_i \nu_im_i} = \frac{\varphi_m}{\varphi_{\pm 2}^*} \quad\text{and}\quad \frac{\gamma_{-m}}{\gamma_{-2}} = \frac{\nu_2m_2^*}{\sum_i \nu_im_i} = \frac{\varphi_m}{\varphi_{\pm 2}^*}, \qquad (47)$$

where γ_{+m} and γ_{+2} are the activity coefficients of the common ion in the mixed and the binary (e.g., the standard) isopiestic solution. For electrolyte solutions without an ion in common we can use the above scheme, which gives (for example) in the case of a $CaBr_2$ solution

$$\gamma_{Ca^{2+}} = \gamma_{\pm CaCl_2}^3(3m_{CaCl_2}^*)^3/\gamma_{\pm KCl}^2(2m_{KCl}^*)^2 \cdot 3m_{CaBr_2}^*,$$
$$\gamma_{Br^-} = \gamma_{\pm KBr}^2(2m_{KBr}^*)^2/\gamma_{\pm KCl}3m_{CaBr_2}^* \cdot 2m_{KCl}^*. \qquad (48)$$

We have calculated[53,54] the activity coefficients of the separate ions in binary solutions of various alkali and alkaline-earth metal halides. The calculations were tested by the scheme used for the osmotic coefficients, but in this case the root mean square values were obtained from pairs of results (because the osmotic coefficients of the ions are additive, and the activity coefficients are multiplicative). The deviation of the calculated mean ionic activity coefficients from the tabulated values[46] was within 1–3% for electrolytes without an ion in common with the standard (potassium chloride).

Bates and coworkers[55] used Robinson and Stokes' hydrate theory to calculate the activity coefficients of separate ions for several solutions of electrolytes. Their results are consistent with ours[54].

For $a_w \to 1$ Raoult's law gives[56]

$$\nu_1m_1^* = \nu_2m_2^* = \sum_i \nu_im_i.$$

Using this expression we find from Eqn.(47) that in very dilute solutions the activity coefficients of the separate ions are a function only of the total ionic concentration, i.e. the

rule of constant water activity becomes an ionic concentration rule[52] reminiscent of Lewis' ionic strength rule but relying on stricter thermodynamic foundations.

Assuming the sulphuric acid–lithium hydrogen sulphate–water system to be isoactive, and assuming equality of the osmotic coefficients of the ions in the isopiestic solutions, we have calculated[35] from data for binary solutions of sulphuric acid and of lithium chloride respectively the dependence of the activity of water on the concentration of lithium hydrogen sulphate (which had not been reported previously). Subsequently[37] the experimental results were compared with calculations: the deviation was less than 1% for isopiestic concentrations, thus allowing all the thermodynamic functions of the system to be calculated by the isoactive solution theory.

If the inter-ionic interactions in the solutions being compared are specific to different extents, more exact values of the osmotic coefficients and of the activity coefficients of the separate ions can be obtained by using quaternary reciprocal systems. Using Eqn.(34) to express the relationship between the osmotic coefficients of 1–1 electrolytes (including the osmotic coefficients of the separate ions) we obtain[24]

$$2\varphi^*_{AM} + 2\varphi^*_{BN} - 2\varphi^*_{AN} - 2\varphi^*_{BM} = ({}^M\varphi^*_A - {}^N\varphi^*_A) + \\ + ({}^B\varphi^*_N - {}^A\varphi^*_N) + ({}^N\varphi^*_B - {}^M\varphi^*_B) + ({}^A\varphi^*_M - {}^B\varphi^*_M) = 2A.$$

Averaging gives

$${}^A\varphi^*_M - {}^B\varphi^*_M = {}^1/_2 A, \qquad (49)$$

where A has the same significance as in Eqn.(39). In the absence of chemical specificity $A = 0$, and Eqn.(49) reduces to equality of the osmotic coefficients of the ions in isopiestic solutions.

A similar averaging is possible for the activity coefficients of individual ions[24]. In this case we write, using the same scheme, an expression relating the logarithms of the activities of the binary electrolytes having identical solvent activities, and also the corresponding expression in terms of the activity coefficients of the separate ions. The same formula for the activity coefficients of the separate ions can be obtained from Eqn.(42) by treating the ions as separate components:

$$\ln \frac{{}^A\gamma^*_M}{{}^B\gamma^*_M} = \ln \frac{m^*_{BM}}{m^*_{AM}} + \frac{1}{4} \ln \frac{a^*_{AM} a^*_{BN}}{a^*_{AN} a^*_{BM}}. \qquad (50)$$

In the absence of chemically specific interactions the expression under the logarithm in the term on the right becomes unity, and formula (50) reduces to (47).

Undoubtedly, the most accurate and general of these equations is[52]

$$\frac{\gamma_{+m}}{\gamma_{+s}} = \frac{\nu_s m^*_s}{\sum_i \nu_i m_i} e^{\Delta} = \frac{\varphi_m}{\varphi_{+s}} e^{\Delta},$$

where Δ is the integral of McCay and Perring's equation for the mixed solution. Extensive information on isopiestic equilibria in ternary solutions with a common ion is available in the literature, and therefore the quantity Δ can be evaluated easily in most cases.

VII. DEVIATIONS FROM IDEAL MIXING IN ISOPIESTIC SOLUTIONS OF ELECTROLYTES

Ideal mixing is a limiting case: all real mixing processes must deviate from ideality to some extent. Aqueous solutions of electrolytes have many features in common, and therefore there is a very large number of pairs of binary solutions which under isopiestic conditions can be mixed with deviations small enough to be ignored. However, mixing operations requiring correction for non-ideality are far from being exceptional. Nevertheless, non-ideal behaviour in mixed systems does not exclude the possibility of limiting cases: for example, in solutions which are dilute with respect to one of the components.

The isotherm–isobars of water in systems with specific interaction between the electrolytes (Figs.1 and 2) are not rectilinear. Substantial curvature of the isotherm–isobars in these systems is usually ascribed to complex formation[57–60], and the curvature is taken as a measure of the intensity of the interactions in the system[61–65]. Even the composition of any compound formed in the mixed solution can be established from the geometry of the isopiestic diagrams[59,60]. We shall examine first of all the general characteristics of the deviations from ideality.

As in the case of mixing individual components, the deviations from ideality in our case can be characterised by excess functions, activity coefficients, and empirical parameters.

Extensive investigations of ternary water–salt systems by Kirgintsev and Luk'yanov, which we have not attempted to list comprehensively among our references[61–65], have shown that the majority of curvilinear isobar–isotherms can be described by the equation

$$1/m = \frac{1}{m^*_1} x + \frac{1}{m^*_2}(1-x) + bx(1-x), \qquad (51)$$

where x is the mole fraction of one of the two electrolytes, and b is an empirical parameter depending on the activity of water and on the concentrations of the components. It follows from (51) that the reciprocal of the total molality is a quadratic function of the composition, in keeping with Robinson's treatment[66].

When $b = 0$ Eqn.(51) reduces to Zdanovskii's law (ideal mixing); when $b > 0$ the system shows positive deviations from ideal mixinge, and when $b < 0$ it shows negative deviations. Inserting Eqn.(51) under the integral in McCay and Perring's equation defines the activity coefficients of the components of the mixture. (The properties of the quantity b and its use in thermodynamic calculations are discussed in detail in Ref.2.) Since our work was based on relationships between osmotic coefficients, we proposed[17,20] that the deviations should be discussed from the standpoint of Eqn.(4). For a real mixture of two electrolytes we have

$$\varphi(a_w, y) = \varphi_1^* y_1 + \varphi_2^* y_2 + \Delta$$

or

$$\varphi(a_w, y) = \varphi_1^* y_1 + \varphi_2^* (1-y_1) + \beta_0 y_1 (1-y_1), \qquad (52)$$

where

$$\Delta = \beta_0 y_1 y_2 = \beta_0 y_1 (1-y_1).$$

This formulation of the deviations from isoactivity allows for the interactions in the system in terms of the activity of water, which is the criterion for isopiesticity of the solutions, and it permits extrapolation to zero concentration of the electrolytes in calculations of the activity coefficients of the components.

When $\beta_0 = 0$ Eqn.(52) becomes indistinguishable from the ideal mixing condition (4). If $\beta_0 > 0$ the system shows positive deviations, suggesting an increase in osmotic properties on mixing, such as would result from increased dissociation of the electrolytes in the mixture as compared with their respective binary solutions. This case is seldom met, and the deviations are usually small. Negative deviations ($\beta_0 < 0$), due to association in the mixed electrolytes, are far more common. Large negative deviations arise from complex formation. Association lowers the osmotic properties of the mixture, and in order to maintain isopiesticity with the

binary solutions the total concentration of electrolytes in the mixture must be increased.

The quantity β_0 is a measure of the interactions in the ternary solution. In general β_0 depends on the activity of water and on the concentration ratio of the electrolytes. For small values of β_0 we only need to consider the effect of water activity, but when the deviations are large we must consider also the effect of solution composition on β_0. Series expansion in powers of the activity of water gives

$$\beta_0 = -\beta_{01}(\ln a_w) + \beta_{02}(\ln a_w)^2 - \ldots \quad (53)$$

In most cases we do not need to go beyond a linear dependence of β_0 on $\ln a_w$, but in some systems a very complex relationship is observed. For example, in mixtures of nickel, cobalt, or copper chloride with lithium chloride[20] β_0 increases at first, going through a maximum, and then decreases and even changes sign: in other words, deviations from Zdanovskii's law of either sign can take place in these systems, depending on the activity of the water. Composition-independence of the parameter β_0 is recognised by the symmetry of the Δ function (Fig.7).

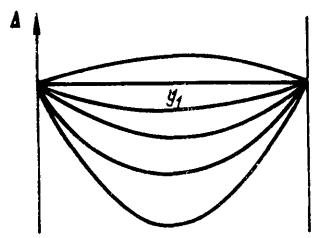


Figure 7. Deviations from isoactivity in ternary water–salt systems.

Whereas the magnitude of β_0 defines the intensity of the interaction, the position of the maximum of the Δ function gives an indication of the composition of the compounds formed in solution. We have used this method to determine, for example, the compositions of the complexes of nickel, cobalt, and copper in chloride and sulphate solutions[20,67,68]. A method of calculating the stability constant of the complex (when only one complex is formed in the solution) was also developed and applied to mixtures of nickel or cobalt nitrate and urea solutions[69]. Results consistent with other methods were obtained.

Experimental determination of Δ or β_0 allows calculation of the excess Gibbs free energies with respect to ideal mixing of the isopiestic solutions ($\Delta G_M^E i$). We have calculated $\Delta G_M^E i$ from measurements of the activity of the solvent only[21,70] by using Scatchard's method[71,73], developed for the isomolal mixing of solutions of 1–1 electrolytes:

$$\Delta G_M^{Ei} - m\partial\Delta G_M^{Ei}/\partial m = -2\Delta RTm.$$

For electrolytes of any valency type this expression becomes (putting $\Sigma\nu_i m_i = \nu_1 m_1 + \nu_2 m_2$)

$$\Delta G_M^{Ei} - \sum \nu_i m_i \frac{\partial \Delta G_M^{Ei}}{\partial \sum \nu_i m_i} = -\Delta RT \sum \nu_i m_i. \quad (54)$$

After converting (54) into

$$-\left(\sum \nu_i m_i\right)^2 \left(\frac{\partial \Delta G_M^{Ei} / \sum \nu_i m_i}{\partial \sum \nu_i m_i}\right)_{\Sigma \nu_i m_i} = -\Delta RT \sum \nu_i m_i$$

we obtain

$$\Delta G_M^{Ei} = \sum \nu_i m_i RT \int_0^{\Sigma \nu_i m_i} \frac{\Delta}{\sum \nu_i m_i} \mathrm{d} \sum \nu_i m_i.$$

Combining this equation with (52) gives

$$\Delta G_M^{Ei} = y_1(1-y_1) RT \sum \nu_i m_i \int_0^{\Sigma \nu_i m_i} \frac{\beta_0}{\sum \nu_i m_i} \mathrm{d} \sum \nu_i m_i. \quad (55)$$

In this expression the excess Gibbs free energy with respect to the isoactive solutions has the dimensions of energy per 1000 g H_2O. We write

$$\beta_0 = \beta'_{01}\left(\sum \nu_i m_i\right) + \beta'_{02}\left(\sum \nu_i m_i\right)^2 + \cdots \quad (56)$$

and, combining (55) and (56), we find

$$\Delta G_M^{Ei} = y_1(1-y_1) RT \left(\sum \nu_i m_i\right)^2 \left[\beta'_{01} + \frac{1}{2}\beta'_{02} \sum \nu_i m_i + \cdots\right] \quad (57)$$

If we retain only the first-order term (i.e. $\beta_0 = \beta'_{01} \Sigma \nu_i m_i$) we have

$$\Delta G_M^{Ei} = \beta_0 y_1(1-y_1) RT \sum \nu_i m_i = \Delta RT \sum \nu_i m_i. \quad (58)$$

Using the relationship between β_0 and b,

$$\beta_0 = -55.51 \ln a_w b\left(\frac{\nu_1 x_1 + \nu_2 x_2}{\nu_1 \nu_2}\right),$$

we obtain an expression for the excess Gibbs free energy with respect to the isoactive solution in terms of the quantity b:

$$\Delta G_M^{Ei} = -x_1(1-x_1) RTmb \cdot 55.51 \ln a_w. \quad (59)$$

In Eqn.(55) the independent variable is the total ionic molality of the mixed solution. It is sometimes convenient to use the activity of water as the independent variable. An appropriate change of variables gives

$$\Delta G_M^{Ei} = y_1(1-y_1) RT \sum \nu_i m_i \int_0^{\ln a_w} \frac{\beta_0}{\ln a_w} \mathrm{d} \ln a_w. \quad (60)$$

Allowing for the dependence of β_0 on the activity of water [Eqn.(53)] we arrive at

$$\Delta G_M^{Ei} = y_1(1-y_1) RT \sum \nu_i m_i \left[\beta_{01}(-\ln a_w) + \frac{1}{2}\beta_{02}(-\ln a_w) + \cdots\right]. \quad (61)$$

Under conditions which justify the approximation $\beta_0 = -\beta_{01} \ln a_w$ we revert to Eqn.(58).

We have used these equations to calculate the excess Gibbs free energies for alkali and alkaline-earth metal halides mixed with cobalt, nickel, and copper chlorides[20] and for alkali metal halides mixed with cobalt, nickel, and alkali metal nitrates[74]. Concurrent measurements of the termal effects in mixing (by Karapent'yants and coworkers[49,75]) have allowed the entropic contributions to be evaluated in most of the mixed solutions.

The most revealing method of expressing the deviations from isoactivity is in terms of the activity coefficients (which are thermodynamic properties of the individual components). A formula for the activity coefficients, obtained from the McCay and Perring equation (41), can be used in conjunction with the expression for the osmotic coefficients.

Eqn.(52) for the osmotic coefficient of the mixed solution can be written as a quadratic function, analogous to (39):

$$\varphi_{(a_w, y)} = Ay^2 + By + C, \quad (62)$$

where $A = -\beta_0$. The difference between this expression and (39) is that the coefficients which appear in (62) can be determined experimentally. In Eqn.(39) they are calculated from the osmotic coefficients of the binary isopiestic solutions. Thus, solution of Eqn.(41) involves operations analogous to those applied to the quaternary reciprocal systems.

By combining Eqn.(62) with the empirical relationship (53) we obtain the following formulae for the activity coefficients:

$$\ln\gamma_1 = \ln\frac{\nu_1 m_1^{\circ}\gamma_1^{\circ}}{\nu_1 m_1 + \nu_2 m_2} + (1-y_1)^2\left[-\beta_{01}\ln a_w + \frac{1}{2}\beta_{02}(\ln a_w)^2 - \cdots\right], \quad (63)$$

$$\ln\gamma_2 = \ln\frac{\nu_2 m_2^{\circ}\gamma_2^{\circ}}{\nu_1 m_1 + \nu_2 m_2} + (1-y_2)^2\left[-\beta_{01}\ln a_w + \frac{1}{2}\beta_{02}(\ln a_w)^2 - \cdots\right].$$

The function β_0 is often linearly related to $\ln a_w$ and independent of composition, allowing the terms in β_{02} to be ignored. Comparing these expressions for the activity coefficients of the components with the excess Gibbs energy [Eqn.(58)] calculated for 1000 g of water and for 1 mole of electrolyte mixture we find

$$g_M^{E_i} = \Delta\mu_1 y_1 + \Delta\mu_2 y_2 = y_1\ln\frac{\gamma_1}{\gamma_1^{\circ}} + y_2\ln\frac{\gamma_2}{\gamma_2^{\circ}}. \quad (64)$$

where $\Delta\mu_i$ is the change in chemical potential of the component with respect to the isoactive mixture of electrolytes, and γ_i and γ_i° are the activity coefficients of the i-th electrolyte in the real solution and in the model solution for which Zdanovskii's law is valid.

The advantages of using the osmotic coefficients in the integration of the McCay and Perring equation include more accurate extrapolation to the region of infinite dilutions, since when $a_w \to 1$ we have $\beta \to 0$, i.e. in the case of electrolyte solutions of any valency type the functional dependence of ϕ under isopiestic conditions tends towards Eqn.(4) at high dilutions. It was found experimentally that for $\beta_0 \leq 0.05$ the errors in the calculation of the activity coefficients are less than 1%. The deviations from the limiting expressions (39) for mixtures of electrolytes without a common ion was estimated[51] in terms of the quantities β_0' and b' by using the expressions

$$(\varphi)_{a_w} = Ax^2 + Bx + C + \beta_0' x(1-x)$$

and

$$1/m = A'x^2 + B'x + C' + b'x(1-x). \quad (65)$$

If $b' = D + Ea_w$, integration of the McCay–Perring equation together with Eqn.(65) gives the following formula for the activity coefficients:

$$\ln\gamma_1 = \ln\frac{m_1^{\circ}\gamma_1^{\circ}}{m_1 + m_2} - (1-x_1)^2\left[\ln\frac{a_1^{\circ}a_4^{\circ}}{a_3^{\circ}a_3^{\circ}} + K\ln a_w\right], \quad (66)$$

where

$$K = (D+E)/0{,}018.$$

The deviations of other thermodynamic functions from isoactivity (e.g. ΔH or ΔV) are best determined directly.

From the experimental point of view the isopiestic method of investigation is not a high-sensitivity method, because all the functions are defined in terms of the activity of the solvent, whose concentration in most cases is substantially greater than the concentration of the solutes. The sensitivity decreases markedly as the electrolyte concentration decreases. An attempt was made[77] to determine the excess enthalpy from the temperature dependence of the excess Gibbs energy, but the results had a large scatter and could only be accepted as tentative.

To conclude this Section we shall dwell on real mixed solutions of electrolytes in which one electrolyte is present at low concentration. In view of the analogy between Zdanovskii's and Raoult's laws we could expect an expression similar to Henry's law to apply to real mixed systems including the micro-component *1*. By using the Gibbs–Duhem equation, and assuming the following expression for the activity coefficient of the micro-component in the ternary solution:

$$\gamma_1 = \frac{\nu_1 m_1^{\circ}\gamma_1^{\circ}}{\nu_2 m_2} e^{l_1/\nu_1 RT}, \quad (67)$$

(where l_1 is an energy parameter depending only on the activity of the water and therefore having the significance of an excess function), we replaced[76] Zdanovskii's law (which is obtained when Mikulin's equation is used) by the expression

$$1 - \frac{m_1}{m_1^{\circ}} - \frac{m_2}{m_2^{\circ}} = -0.018\frac{m_1}{RT}\frac{\mathrm{d}\,l_1}{\mathrm{d}\ln a_w}. \quad (68)$$

This equation gives the relationship between (dm/dx) and $dl_1/d\ln a_w$, where $x = m_1/m$:

$$m\left(\frac{1}{m_2^{\circ}} - \frac{1}{m_1^{\circ}}\right) + \left(\frac{x}{m_1^{\circ}} + \frac{1-x}{m_2^{\circ}}\right)\left(\frac{\partial m}{\partial x}\right)_{a_w} = \frac{1}{RT}\frac{\mathrm{d}\,l_1}{\mathrm{d}\ln a_w}\left[x\left(\frac{\partial m}{\partial x}\right)a_w + m\right]. \quad (69)$$

From Eqn.(69) we can obtain the dependence of l_1 on a_w by using isopiestic measurements on ternary systems. It is clear from Eqn.(68) that at constant water activity the deviation from Zdanovskii's law (given by the right-hand side of the equation) is proportional to the molality of the micro-component. Denoting this deviation by bm_1 we can write

$$1/m = x_1(1/m_1^{\circ} + b) + x_2/m_2^{\circ}. \quad (70)$$

Thus the contribution of the micro-component to the reciprocal total molality remains proportional to the mole fraction, but the proportionality coefficient is no longer equal to the reciprocal isopiestic concentration, and depends also on the differential $dl_1/d\ln a_w$. This is where the analogy between our expression and Henry's law appears. The quantity b is a parameter of Eqn.(51), which reduces to Eqn.(70) when $x_1 \ll 1$. In the absence of specific interactions between the dissolved electrolytes Eqn.(67) simplifies to Eqn.(32).

VIII. SALTING-OUT IN EXTRACTION SYSTEMS

Salting-out effects provide one of the most important applications of the theory of isoactive mixed solutions of electrolytes. This was realised by Zdanovskii, Mikulin, and Kirgintsev, all of whom made important contributions in this area. Their work was aimed mainly at the salting-out of electrolytes into a solid phase, i.e. at determining the solubility of some electrolytes in the presence of others. In this review we shall confine our attention to the salting-out problem in extraction systems, where the substance to be separated is distributed between two liquid phases.

The salting-out effect is directly related to the effective concentration (activity) of the solvent. It manifests itself as a change in the activity coefficient of the component being salted out, and therefore salting-out problems can be solved like other problems in the theory of multi-component solutions. The effectiveness of the salting-out agent is determined by its tendency to become hydrated. Ionic hydration is often thought to be determined by the charge and the radius of the ion. However, this view is too simple, and we must think of hydration as the result of a large number of specific properties of the substance whose overall effect

cannot be ascribed merely to the charge and the size of the ion. In recent years the hydration propensity of electrolytes has been quantified in calculations of activity coefficients by using hydration numbers, which give a very good description of specific properties because they are, to some extent, a derived characteristic[46,78]. We know, nevertheless, that experimental values of the hydration number are strongly dependent on the method of measurement, and can vary by a large factor. Furthermore, methods of calculating salting-out effects by relying on constant parameters cannot reflect changes in hydration with concentration, which are characteristic of electrolyte solutions. Hence, these methods can give only a qualitative estimate of changes in systems containing a salting-out agent.

Harned's coefficient is often used as a criterion for salting-out effects. However, Harned's coefficient can be obtained only if experimental data are available for the multi-component system of interest. Furthermore, it is extremely sensitive to the uncertainties in the determination of the activity coefficients. For example, Vdovenko and Ryazanov[79] have shown that an error of 2% in the activity coefficients can produce deviations of up to 10% in the Harned coefficient. We should note that since the "ionic strength" concept lacks strict thermodynamic foundations all attempts at calculating the Harned coefficient theoretically must continue to be unsuccessful.

We have previously suggested[4] the use of the molal mean ionic isopiestic osmotic coefficient as a criterion of the effectiveness of salting-out agents. The osmotic coefficient is, of course, a thermodynamic parameter of the electrolyte solution which characterises its ability to take up water and embodies all the individual properties of the solution. We should stress that the osmotic coefficient takes account also of any interactions between the ions and the molecules of the dissolved electrolyte. The osmotic coefficients of binary solutions have been determined over a wide range of concentrations for most electrolytes of interest and to a high precision. They are tabulated in Robinson and Stokes' monograph[46]. The most significant advantage of the osmotic coefficient as a criterion of salting-out effectiveness is its direct relationship to the theory of mixed isoactive solutions outlined above. The osmotic coefficient, being a thermodynamic criterion of salting-out, can be used as a reference standard for the salting-out parameters given by other solution theories. By combining Mikulin's equation (25) with Eqn.(1) we obtain Eqn.(26), from which it follows that the activity coefficients of the components (or their salting-out properties) are determined exclusively by the osmotic coefficients.

To determine the efficiency of a salting-out agent we simply plot the function $a_w = f(\nu m)$ for the appropriate binary solutions (see Fig.3), which follows from Eqn.(1) and from which it is clear that the relative position of the curves is determined only by the osmotic coefficients of the electrolytes. The higher the osmotic coefficient (or the steeper the curve), the more effective will be the electrolyte as a salting-out agent. For example, magnesium chloride at low ionic concentrations is a less effective salting-out agent than nitric acid. However, the curves intersect at $\nu m \cong 3.3$, and at the higher ionic concentrations magnesium chloride becomes a stronger salting-out agent than nitric acid. This inversion of the relative effectivenss of pairs of electrolytes is encountered fairly often. We note that the plot shown in Fig.3 can be used at the same time to determine the isopiestic concentrations, which are needed to calculate the activity coefficients by Mikulin's equation in accordance with Zdanovskii's law.

Calculations of the salting-out effect (W) can be classified into three possible cases[80]. In the first case addition of the salting-out agent affects the thermodynamic activity of the substance to be separated, but saturation is not reached. The system remains homogeneous, and the concentrations in the phase are unchanged. For a non-electrolyte we can write

$$a_{ns} = m\gamma_{ns};\ a_{ws} = m\gamma_{ws},$$
$$W_a = a_{ws}/a_{ns} = \gamma_{ws}/\gamma_{ns}, \qquad (71)$$

and for an electrolyte

$$a_{ns} = \nu_+^{\nu_+}\nu_-^{\nu_-} m^{\nu}\gamma_{\pm ns}^{\nu},\quad a_{ws} = \nu_+^{\nu_+} m^{\nu_+}(\nu_- m + \nu_{-s} m_s)^{\nu_-}\gamma_{\pm ws},$$
$$W_a = \frac{a_{ws}}{a_{ns}} = \left(\frac{\gamma_{\pm ws}}{\gamma_{\pm ns}}\right)^{\nu}\left(1 + \frac{\nu_{-s} m_s}{\nu_- m}\right)^{\nu_-}, \qquad (72)$$

where a_{ws}, a_{ns}, and γ_{ws}, γ_{ns} are the activities and activity coefficients of the components with and without the salting-out agent respectively, m is the concentration of the main solute, m_s is the concentration of the salting-out agent, and ν, ν_+, and ν_- are the stoichiometric coefficients of the electrolyte, the cation, and the anion respectively.

It follows from (71) and (72) that during salting-out in a homogeneous system the salting-out effect W_a for the non-electrolyte is determined only by the change in the activity coefficients, whereas in the case of the electrolyte the change in concentration of the like ion (in our case, the anion) also has an effect. If the solutions are isoactive the activities of the main electrolyte and the salting-out effects are easily calculated by using the theory of mixed isoactive solutions to obtain the activity coefficients.

The second case relates to salting-out in a heterogeneous system, when the solution is in equilibrium with the main component in the pure state. Addition of the salting-out agent in this case does not alter the activity of the main compound, but it alters its concentration (i.e. the solubility). For a non-electrolyte we have

$$m_{ns}\gamma_{ns} = m_{ws}\gamma_{ws} \text{ and } W_m = m_{ns}/m_{ws} = \gamma_{ws}/\gamma_{ns}, \qquad (73)$$

and for an electrolyte

$$\nu_+^{\nu_+}\nu_-^{\nu_-} m_{ns}^{\nu}\gamma_{\pm ns}^{\nu} = \nu_+^{\nu_+} m_{ws}^{\nu_+}(\nu_- m_{ws} + \nu_{-s} m_s)^{\nu_-}\gamma_{\pm ws}^{\nu},$$
$$W_m = \frac{m_{ns}}{m_{ws}} = \frac{\gamma_{\pm ws}}{\gamma_{\pm ns}}\left(1 + \frac{\nu_{-s} m_s}{\nu_- m_{ws}}\right)^{\nu_-/\nu}. \qquad (74)$$

If the mixed solutions are isoactive we can easily calculate the solubility m_{ws} in the presence of the salting-out agent from Eqn.(74) after determining the activity coefficients of the main compound in the mixed solution by the above formulae. The activity coefficients of non-electrolytes and gases in solutions are inversely proportional to the solubility. If these solutes are indifferent to the salting-out electrolyte we may assume that the solubility (S_0) is proportional to the activity of the solvent, and re-write Eqn.(73) as

$$\ln\frac{S_0}{S} = \ln\frac{m_{ns}}{m_{ws}} = -\ln a_S. \qquad (75)$$

Using Eqn.(1) we obtain[81,82]

$$\lg\frac{S_0}{S} = K_\varphi \nu_s m_s \varphi_s.$$

This formula is the analogue of Sechenov's equation[83], but it differs from it by taking account both of the ionic concentration of the salting-out agent and of its affinity for the solvent (ϕ_S). The constant K_ϕ should be (in the ideal case) independent of the nature of the salting-out electrolyte.

The third salting-out case is distinguished by the fact that addition of the salting-out agent to one phase alters the concentrations of the main substance in both phases. Salting-out in extraction systems is of this type. Whereas in the

first case the concentration was constant, and in the second case the activity, in this case the constant parameter is the distribution constant of the main substance between the phases, given by the ratio of the activities in the two phases[81,82]:

$$K=\bar{a}_{ns}/a_{ns}=\bar{a}_{ws}/a_{ws} \qquad (76)$$

The salting-out effect W_D is the numerical factor by which the distribution coefficient $D=\bar{m}/m$ is increased. For the distribution of a non-electrolyte we have

$$W_D=\frac{D_{ws}}{D_{ns}}=\frac{\bar{m}_{ws}m_{ns}}{m_{ws}\bar{m}_{ns}}=\frac{\gamma_{ws}}{\gamma_{ns}}\cdot\frac{\bar{\gamma}_{ns}}{\gamma_{ws}}. \qquad (77)$$

In the case of electrolytes (assumed undissociated in the organic phase) we obtain

$$W_D=\left(\frac{m_{ws}}{m_{ns}}\right)^{\nu-1}\left(1+\frac{\nu_{-s}m_s}{\nu_-m_{ws}}\right)^{\nu_-}\left(\frac{\gamma_{\pm ws}}{\gamma_{\pm ns}}\right)^{\nu}\frac{\bar{\gamma}_{ns}}{\bar{\gamma}_{ws}}. \qquad (78)$$

Thus, in extraction systems the overall salting-out effect is determined as much by changes in the organic phase as by those in the phase containing the salting-out agent. Furthermore, in the case of electrolytes the effect of the salting-out agent is not only to increase the distribution coefficient but also to alter the shape of the extraction isotherm. Without the salting-out agent the distribution coefficient of the main substance (in the absence of dissociation in the organic phase) tends towards zero as the dilution is increased. In the presence of the salting-out agent the expression for the distribution coefficient becomes

$$D_{ws}=K\nu_+^{\nu_+}m_{ws}^{\nu_+-1}(\nu_-m_{ws}+\nu_{-s}m_s)^{\nu_-}\gamma_{\pm ws}^{\nu}/\bar{\gamma}_{ws}, \qquad (79)$$

where $m_{ws}^{\nu_+-1}=1$ for electrolytes in which the stoichiometric coefficient of the cation is $\nu_+=1$ (which is true of many electrolytes). Therefore when $m_{WS}\to 0$ the distribution coefficient D_{WS} tends towards a constant, non-zero value. This effect has great practical importance in extraction by "neutral" extractants, especially for trace amounts of electrolytes.

Since the extraction of inorganic substances is often due to chemical interaction between these substances and the extractant we can obtain[81,82] equations for the salting-out effect corresponding to different extraction mechanisms[84-86] by equating constants of the extraction reaction with and without the salting-out agent. For example, in the case of molecular extraction, and negligible dissociation in the organic phase, typical of extraction by "neutral" extractants

$$n\bar{A}+B\rightleftarrows\bar{A}_nB,$$

we have obtained the expression[80-82]

$$W_D=\left(\frac{m_{Bws}}{m_{Bns}}\right)^{\nu-1}\left(1+\frac{\nu_{-s}m_s}{\nu_-m_{Bws}}\right)\left(\frac{\gamma_{\pm Bws}}{\gamma_{\pm Bns}}\right)^{\nu}\cdot\frac{\bar{\gamma}_{A_nB_{ns}}}{\gamma_{A_nB_{ws}}}\left(\frac{\bar{a}_{Aws}}{a_{Ans}}\right)^{n}. \qquad (80)$$

This expression shows that allowance must be made for changes in the activity coefficient of the resulting complex and in the activity of the extractant caused by the addition of the salting-out agent to the extraction system. Eqn.(80) is most conveniently used in a logarithmic form[80], in which the various contributions to the overall salting-out effect are additive:

$$\lg W_D=\lg W_c+\lg W_{c.i.}+\lg W_{\gamma\pm}+\lg\bar{W}_\gamma+\lg\bar{W}_A, \qquad (81)$$

where W_C is the concentration effect, $W_{C.i.}$ is the common ion effect, $W_{\gamma\pm}$ is an effect due to changes in the activity coefficients of the electrolyte in the aqueous phase, $\bar{W}_\gamma$ is due to the change in the activity coefficients of the complex in the organic phase, and $\bar{W}_A$ is due to the change in the activity of the extractant. Analogous considerations can be applied to the factors affecting the separation of substances (see Ref.87 for a detailed discussion).

These thermodynamic arguments show that calculations of salting-out effects almost invariably reduce to calculations of changes in the activity coefficients of the main substance in the two phases, though on occasions the activity coefficients of other (interacting) components are also relevant. The other contributions to the overall salting-out effect are relatively easy to calculate. In the case of an isoactive aqueous phase the activity coefficients of the electrolytes can be calculated by the equations given above, whereas the calculation of the activity coefficients of the components in the organic phase often requires additional experiments.

The isopiestic method has been found to be useful also in studies of some properties of the organic phase. For example, experimental determination of the activity coefficients of the components in the mixed solution by the distribution method was shown[88] to be possible if the osmotic coefficients of the substance to be extracted and of the salting-out agent are not very different, especially when the solubility of water in the organic phase is appreciable.

The solubility of water in the organic phase depends not only on the nature of the diluent (extractant) but also on the nature of the substance to be extracted. Water can either decrease or increase the association of the components. However, another general feature is the influence of the water on the standard state in the organic phase in the calculation of the activity coefficients of the components. By applying the Gibbs–Duhem equation to a three-component solution we have shown[89,90] that the degree of hydration of the extractant, complex, or distributed component (m_2) is

$$h=(m_3-m_3^0)/m_2,$$

where m_3 is the concentration of water in the extract, m_3^0 is the solubility of water in the diluent, and for $m_2\to 0$ it is a measure of the effect of water on the activity of component 2 when this component is transferred from its binary solutions to solutions containing water. Furthermore,

$$\ln\frac{a_2^0}{a_2}=h \quad\text{or}\quad \ln\gamma(0)=h, \qquad (82)$$

where a_2^0 and a_2 are the activities of the second component in the pure and in the moist diluent (solvent) respectively, and $\gamma(0)$ is the zeroth activity coefficient, characterising changes of standard state. This expression was later confirmed for a large number of systems. A more detailed account of the effect of water and of ways to allow for it in calculations of the component activities in the organic phase can be found in Refs.89 and 90.

Thus, in extracts where the main contribution to the changes in the activity coefficients is that of hydration these coefficients are easily determined if h is known. An independent determination of the salting-out effect in the organic phase is thus possible.

The contributions of the components to the overall salting-out effect have been determined for several systems with different extractants and extracted substances[91-93], including acids and salts. We shall mention only one example: the extraction of nitric acid by N-dioctylamine in o-xylene[93]. Salting-out by lithium nitrate[93] is illustrated in Fig.8: the effects were determined according to Eqn.(81) for a constant initial acid concentration of 0.25 M. The activity coefficients of nitric acid in the water phase in the presence of the salting-out agent were calculated by Mikulin's equation (25), and the activity of the free extractant was assumed to be equal to its concentration. The ratio of the activity coefficients in the organic phase was determined from the extraction isotherm[94] in terms of the known activities of the acid

in the water phase. It is clear from Fig.8 that all the salting-out effects included in Eqn.(80) play a substantial role in this system. In this case large positive effects are produced by the change in the activity coefficient of the salt formed in the organic phase, due mainly to the increase in the association of the salt with concentration. The common ion effect is even more substantial. All the other effects, including the change in the activity coefficients in the water phase, are negative. Depending on the chosen system, the contributions of the various effects may differ in sign as well as in magnitude.

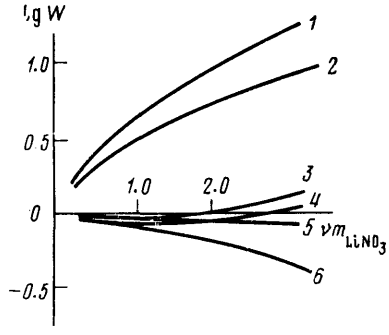


Figure 8. Salting-out effects for nitric acid in the presence of lithium nitrate: *1)* $W_{c.i.}$, *2)* W_D, *3)* $\bar{W}_\gamma$, *4)* W_γ, *5)* W_A, *6)* W_c.

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This review shows that the theory of isoactive solutions is essentially an osmotic theory, since it operates on the osmotic properties of solutions (solvent activity, osmotic acitivities, osmotic coefficients). The validity of isoactive solution theory can no longer be doubted. Experimental studies of mixed solutions at constant activity of the solvent, and isopiestic measurements, have made a valuable contribution to the development of the theory and practice of mixed concentrated solutions.

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The α-Effect in Organic Compounds of Group IVB Elements

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A critical and systematic account is given of the results of studies of the α-effect by physical and chemical methods. The nature of the α-effect, its characteristic features, and its influence on the structure and properties of the corresponding organic compounds of Group IVB elements are discussed.
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I. INTRODUCTION

The mutual influence of the atoms X and E in organic molecules containing the triatomic group $X-\overset{|}{\underset{|}{C}}-E$ does not correspond to their electronegativities and to the inductive effect of the constituents (the geminal interaction effect)[1-5]. Such an effect is shown in virtually all compounds and the atoms E and X can have both unshared electron pairs and vacant orbitals. This non-inductive interaction is usually observed when one compares the properties of the above compounds with isostructural compounds in which E = C or with homologues of type XCH_2CH_2M. We have called[5-8] the non-inductive geminal interaction of a given atom X with an atom E having vacant *d* orbitals in the $X-\overset{|}{\underset{|}{C}}-E$ system the α-effect†. At the present time the problem of the α-effect in an organic compound of Group IVB elements has attracted the attention of many investigators[9] and numerous publications have been devoted to it. Nevertheless the views on the nature of the α-effect and on the very possibility of its occurrence, based on studies using a wide variety of different physical and chemical methods, are extremely contradictory. The methods employed make it possible to observe the geminal interaction effect and to investigate its characteristics, but the majority do not permit the determination of the mechanism of the effect. Therefore almost all the existing hypotheses concerning the nature of the α-effect do not have a serious basis.

Some investigators (see below) base their views on individual experimental data which are consistent with ideas concerning the dominant inductive interaction of the atoms E and X and the problem of the occurrence of the intramolecular non-inductive interaction of geminal atoms is still regarded as controversial. There also exists a view that the α-effect is not shown in all the compounds containing the $X-\overset{|}{\underset{|}{C}}-E$ group but only in certain molecules of this type.

This indefinite state of the problem of the α-effect led us to write the present review.

†The term "α-effect" sometimes has another significance. For example, it is used in the interpretation of the anomalous reactivity of hydrazine derivatives (see, for example, Edwards and Pearson[10] and Grekov and Veselov[11]).

II. CHEMICAL MANIFESTATIONS OF THE α-EFFECT

The anomalous (i.e. inconsistent with the inductive influence of the atom E or a substituent in which it is included) properties of compounds containing the group $\overset{|}{\underset{|}{X-C-E}}$ were observed a long time ago. Thus, as early as the 1950's, it was noted that chloromethyltrimethylsilane is much more reactive in nucleophilic substitution reactions than its carbon analogue, while it is inert with respect to electrophiles (see, for example, George et al.[12] and Andrianov and Petrashko[13]). This was explained by the steric characteristics of the group $CH_2Si(CH_3)_3$ and its comparatively pronounced electron-accepting properties[14]. The electronegativity (EN) of this group, determined by the Kharash method, proved to be higher than that of the alkyl groups $n-C_6H_{13}$, CH_3, and $CH_2C(CH_3)_3$ but lower than that of the phenyl group. The expectedly high electronegativity of this group was attributed to the electronic unsaturation of the silicon atom[14]. The unusual influence of the silicon atom in compounds of the type $XCH_2Si(CH_3)_3$ (X = Cl or I) on their reactivity has been called the "α-silicon effect".[14]

In contrast to β- and γ-chloroalkylchlorosilanes, chloromethylchlorosilanes undergo the Friedel–Crafts reaction with difficulty[15-21], which indicates a reduced electron density at the chlorine atom in the group $ClCH_2Si\lesssim$. The replacement of the chlorine atom linked to the silicon atom by an alkyl group as a rule increases the reactivity of the compound. For example, $ClCH_2(CH_3)SiCl_2$ is more reactive in this reaction than $ClCH_2SiCl_3$.[21].

The relatively high reactivity of $ClCH_2Si(CH_3)_3$ in the reaction with KI (higher by a factor of 16 than for $n-C_4H_9Cl$, by a factor of 15 than for $n-C_3H_7Cl$, and by a factor of 8 than for C_2H_5Cl) was explained by the stabilisation of the transition state as a result of the interaction of the approaching iodide ion with the vacant 3*d* orbitals of the silicon atom and with the carbon atom[22-24]. It has been suggested that the leaving chloride atom thus interacts with the Si and C atoms[22,25-27]:

$$ClCH_2Si(CH_3)_3 + {}^{-}I \rightleftarrows CH_2\begin{matrix}\diagup Cl\\ \\ \diagdown I\end{matrix}Si(CH_3)_3 \rightleftarrows ICH_2Si(CH_3)_3 + Cl^{-}\ .$$

An analogous mechanism has been postulated for the reaction of chloromethyltrimethylsilane with the SCN^- ion in acetone and with the $C_2H_5O^-$ ion in ethanol[22,25,28]. The reactivity of $ClCH_2Si(CH_3)_3$ with respect to the $C_2H_5O^-$ ion is somewhat lower than that of $n-C_4H_9Cl$. However, it

would be lower still were it not for the possibility of the coordination interaction of the type indicated above[25,29]. It has been shown that $ICH_2Si(CH_3)_3$ is less reactive in the exchange with the I^- ion in ethanol than $n\text{-}C_3H_7I$.[14,25]. In the absence of coordination interaction, one would expect that iodomethyltrimethylsilane is still less reactive[25].

In bimolecular nucleophilic substitution reactions with KI and KSCN the chlorine atom in chloromethyltrimethylsilane is much more mobile than in γ-chloropropyltrimethylsilane[12,30], which is consistent with the electron-accepting properties of the trimethylsilyl group. On the other hand, in the interaction of chloromethyl- and γ-chloropropyl-trichlorosilanes with alcoholic alkali, the chlorine atom in the γ-position with respect to the silicon atom is much more mobile[31]. The discrepancy between these results has been explained by the fact that alcoholic alkali is not a reagent characterising the reactivity of the chlorine atom in the C–Cl bond in reactions of organosilicon compounds, because under the influence of alkali on chloromethyltrichlorosilane the reaction involves only the Si–C bond, while the reaction with γ-chloropropyltrichlorosilane involves both the Si–C and the Si–Cl bonds[30].

The exchange reactions between the chloromethyltrimethylgermane and KSCN, $HN(C_2H_5)_2$, and KI are faster than the analogous reactions of chloromethyltrimethylsilane, which shows that the $CH_2Ge(CH_3)_3$ group is more electronegative than $CH_2Si(CH_3)_3$. This is consistent also with the lower basicity constant of $(C_2H_5)_2NCH_2Ge(CH_3)_3$ compared with $(C_2H_5)_2NCH_2Si(CH_3)_3$.[32] The reactivity of chloromethyltrimethylstannane (in reactions of the S_N2 type) with respect to I^- and $C_2H_5O^-$ ions is higher still than those of chloromethyltrimethylsilane and chloromethyltrimethylgermane[25]. On the other hand, the electron-donating properties of the $-E(CH_3)_3$ groups become more pronounced as a function of E in the following sequence: Si < Ge < Sn.[33,34]. Consequently the observed sequence in the variation of the reactivity of compounds of the $ClCH_2E(CH_3)_3$ series (E = C, Si, Ge, or Sn) does not correspond to the inductive effect of the groups $-E(CH_3)_3$. This was explained by the fact that the nucleophilic substitution reactions involving these compounds proceed via the "bridge mechanism" described above, which is most marked in the case of chloromethyltrimethylstannane. In conformity with this, the tin atom exhibits a greater tendency than silicon and germanium atoms to expand its coordination number with formation of pentacoordinate and hexacoordinate complexes[35] and exhibits the smallest steric hindrance to nucleophilic attack because of its large atomic radius[25].

The rate constants for the reaction of chloromethyltrimethylsilane with sodium in the gas phase are greater than for neopentyl chloride and γ-chloropropyltrimethylsilane almost by factors of 15 and 5 respectively, which shows that the negative charge on the chlorine atom in chloromethyltrimethylsilane is smaller than in the compounds with which it has been compared[36].

In the reaction with 80% aqueous ethanol α-halogenoisopropyltrimethylsilanes $X(CH_3)_2CSi(CH_3)_3$ (X = Cl or Br) are much less reactive than their carbon analogues $X(CH_3)_2 \cdot CC(CH_3)_3$ and $XC(CH_3)_3$. This has been explained[37] by the enhanced electron-donating properties of the CH_3 and $C(CH_3)_3$ groups owing to the ability of their C–H and C–C bonds to participate in hyperconjugation (and not by the reduced electron-donating capacity of the trimethylsilyl group). It has also been suggested[37] that the lower reactivity of $Br(CH_3)_2CSi(CH_3)_3$ with respect to aqueous alcohol relative to $Br(CH_3)_2CH$ is caused by steric hindrance to solvation. A greater electron-accepting effect of the $Si(CH_3)_3$ group, compared with hydrogen, which would lead to the observed ratios of the rates of solvolysis of the above compounds is thought to be unlikely[37].

The rate constants for the acid-catalysed hydrolysis of triorganylsilanes $HSiR_3$ are correlated with the inductive Taft constants of the constituents R. However, the rate constant for the hydrolysis of chloromethyldimethylsilane deviates from this correlation, which has been explained[38] by the interaction of the unshared electron pair of the chlorine atom with the vacant *d* orbitals of silicon, described by the resonance structure $Cl^+CH_2=SiR_3$.

The enthalpies of the protonation reactions of the compounds $X(CH_2)_nEH_3$ (E = C or Si; X = Cl or F), calculated by the LCAO-MO method in the CNDO/2 approximation (with and without inclusion in the calculation of the vacant *d* orbitals of silicon), depend greatly on the molecular conformation for E = Si, but are insensitive to conformational changes for E = C. This indicates the occurrence of an intermolecular interaction in organosilicon compounds containing the $X-CH_2-Si$ group which is not characteristic of their organic analogues[39].

The reactivity of fluoromethyltrimethylsilane in the reaction with ethylmagnesium bromide is higher, as for the corresponding chloro-derivative, than that of γ-fluoropropyltrimethylsilane. In both compounds the fluorine atom is more mobile than in n-heptyl fluoride. It has been suggested[40] that this is caused by the "positive inductive influence" of the trimethylsilyl group, which has been shown most markedly in fluoromethyltrimethylsilane. The inertness of the fluorine atom in neopentyl fluoride has been attributed to the steric effect of the t-butyl group[40].

The numerous rearrangements involving the cleavage of the E–C bond and the migration of the substituent X from the carbon atom to the E atom have been explained by the intramolecular interaction between the E and X atoms in the molecules containing the group $X-\overset{|}{\underset{|}{C}}-E$ (E = Si, Ge, or Sn):

$$X-\overset{|}{\underset{|}{C}}-E- \rightarrow X-E+:C\overset{|}{\underset{|}{\ }}.$$

Reactions of this type are observed, for example, in the pyrolysis of organosilicon compounds containing the group $X-\overset{|}{\underset{|}{C}}-Si$ (X = halogen)[41–43]. A similar rearrangement with formation of a carbene takes place in the case of halogenomethylsilanes:

$$XCH_2SiH_3 \rightarrow XSiH_3 + :CH_2 \ (X = F, Cl, I)^{44}.$$

The cleavage of the Si–C bond with migration of the fluorine atom from the α-carbon atom to the silicon atom in the compound $F_2CHCF_2SiX_3$ takes place in the vapour phase at 130–210 °C (X = F) or at 310–370 °C ($X = CH_3$):[45]

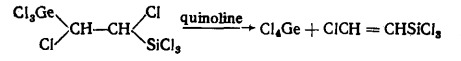
$$F_2CHCF_2SiX_3 \rightarrow \left[F_2CHCF\begin{matrix}\nearrow F\\ \searrow SiX_3\end{matrix}\right] \rightarrow FSiX_3 + :CFCHF_2.$$

The α-decomposition of perhalogeno-derivatives of ethylchlorosilanes at 185 °C proceeds much more readily than the very common β-elimination[46–48]:

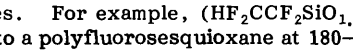
$$Cl_2SiCF_2CFCl_2 \begin{cases} \xrightarrow{\alpha} Cl_2SiF + :CFCFCl_2 \rightarrow CFCl=CFCl & (80\%) \\ \xrightarrow{\beta} Cl_2SiF + F_2C=CCl_2 & (7\%). \end{cases}$$

The pyrolysis of perfluoroalkyltrifluorosilanes proceeds similarly[49]. Similar reactions with liberation of dichlorocarbene are observed in the pyrolysis of Cl_3CSiCl_3 [24,47,50] and Cl_3CSiF_3.[51]

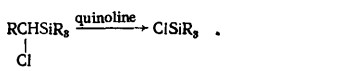
When 1,2-dichloro-2-trichlorogermyl-1-trichlorosilylethane is treated with quinoline, $GeCl_4$ is split off and not HCl. The explanation is that the germanium compounds exhibit a greater tendency towards β-decomposition than their silicon analogues[45]:



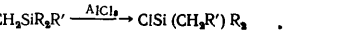
The α-elimination process is responsible for the thermal instability not only of α-fluoroalkylsilanes but also of α-fluoroalkylsiloxanes. For example, $(HF_2CCF_2SiO_{1.5})_n$ is rapidly converted into a polyfluorosesquioxane at 180–200 °C:[52]



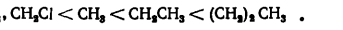
α-Decomposition is also observed in the interaction of α-chloroalkyltrialkylsilanes with quinoline[50]:



In the presence of aluminium chloride trialkylchloromethylsilanes undergo an intramolecular rearrangement[53]:

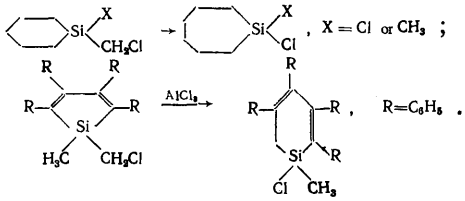


The relative ability of compounds of this type to rearrange increases in the following sequence based on varying R′:

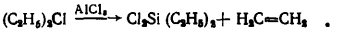


The rearrangement proceeds via a transition state in which both substituents, R′ and Cl, are coordinated to silicon and carbon atoms[54].

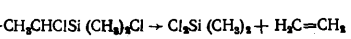
A special case of a rearrangement of this type is the expansion of the silacycloalkane ring[55] and also of the silacyclopentadiene ring[56]:



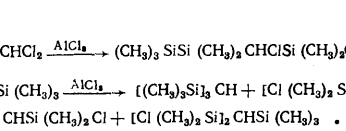
Aluminium chloride causes not a rearrangement but α-decomposition of α-chloroethylsilanes $CH_3CHClSiR_3$:[23,57]



The rearrangement of trialkyldichloromethylsilanes in the presence of $AlCl_3$ proceeds via the mechanism[23,57]



1- and 2-dichloromethylheptamethyltrisilanes also undergo a rearrangement in the presence of $AlCl_3$ with rupture of the Si–Si bond and the migration of chlorine atoms to the silicon atom[59]:

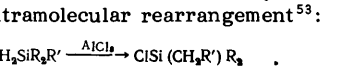


The decomposition of $F_3CSn(CH_3)_3$ with formation of difluorocarbene[60–62] is apparently due to the coordination interaction between the fluorine and tin atoms. The reactivity of the chlorine atom in trialkylchloromethylstannanes[32,60,63,64], which is higher than in the carbon, silicon, and germanium analogues, has been explained by the intramolecular coordination between the Sn and Cl atoms.

Under the influence of bases, trialkylsilylmethanols are very readily converted into the isomeric ethers[65–69]:

It has been suggested that this rearrangement takes place with formation of a bond between the silicon and oxygen atoms in the transition state; the silicon atom then becomes sp^3d-hybridised. Electron-accepting substituents at the silicon atom facilitate the rearrangement, since they promote the delocalisation of the negative charge in the three-membered transition state formed[65]. Such rearrangements are not observed for β- and γ-trialkylsilylalkanols $HO(CH_2)_n \cdot SiR_3$ ($n = 2$ or 3).[70] The thermal rearrangement of alkyl esters of α-trialkylsilylalkanecarboxylic acids, which has no analogy in organic chemistry, has been explained by a similar three-membered cyclic transition state[71].

In the pyrolysis of compounds containing the O–C–Si group the oxygen-containing group migrates from the carbon atom to the silicon atom and a carbene is evolved[72,73]:



$(C_6H_5)_2C(OCH_3)SiR_3$ is cleaved similarly[73].

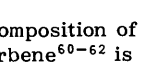
The reactivity of organosilicon and organogermanium compounds of the type XCH_2ER_3 (X = O or S; E = Si or Ge) is largely consistent with the inductive influence of the ER_3 group. Thus, in a reaction with an electrophile (phenyl isocyanate) trimethylsilylmethanol is 6 times more reactive than neopentyl alcohol[74,75], more than 4 times more reactive than butanol[76], and 2.5–3 times more reactive# than methanol[74,75,77]. In its interaction with keten, trimethylsilylmethanol is 3 times more reactive than butanol[76]. The reactivity of trimethylgermylmethanol in these reactions is also significantly higher than those of neopentyl alcohol, methanol, and butanol[78]. The reactivity of alcohols of the $HO(CH_2)_nE(CH_3)_3$ series (E = Si or Ge; $n = 1–4$) in reactions with phenyl isocyanate and keten falls with increase of the number of methylene groups n and, when $n = 3$ and 4, becomes the same as that of butanol[76,78]

In the reaction with phenyl isocyanate[79] the reactivity of trimethylsilylmethanethiol is higher than that of the remaining thiols of the $HS(CH_2)_nSi(CH_3)_3$ ($n = 1–4$) series and butanol.

All these data can be accounted for by the enhanced electron-donating inductive influence of the trimethylsilyl or trimethylgermyl group which decays with increase of the number n.[76,78,79] The decrease of the nucleophilic properties of the thiyl group in mercaptans of the $HS(CH_2)_nSiR_3$ series with increase of n from 1 to 3, observed in the study of the vinylation of these compounds and confirmed by the results of potentiometric titration studies[80], can also be explained by the electron-donating influence of the trialkylsilyl group[80].

III. INVESTIGATION OF THE α-EFFECT BY PHYSICAL METHODS

The vast majority of studies on compounds containing the



grouping (E = Si, Ge, or Sn group) by various physical

The high reactivity of trimethylsilylmethanol in this reaction has also been explained[75] by the electron-accepting properties of the $CH_2Si(CH_3)_3$ group.

methods indicate the anomalous nature of their properties due to the non-inductive influence of the substituents X and E. Nevertheless some of the physical properties of these compounds are consistent with the inductive influence of the E atom (E = Si, Ge, or Sn) or more correctly of the group ER_3 incorporating it on the X atom.

On decrease of the electronegativity of the halogen atom in the sequence X = Cl, Br, I in molecules of the type XCH_2SiH_3, one should expect a decrease of their dipole moments, but in reality the dipole moments of all compounds of this type remain virtually constant. This has been explained[81] by the $(p-d)_\sigma$ or $(p-d)_\pi$ interaction of Si and X atoms not linked directly[81]. The dipole moment of the C–X bond in molecules of the type XCH_2EH_3 for E = Si is much smaller than for E = C. The difference between these dipole moments diminishes on passing from X = Cl to X = Br and I. It has been suggested[81] that this corresponds to a weakening of the interaction of the silicon and halogen atoms with decrease of the electronegativity of the halogen. Accordingly, if it is assumed that the dipole moments of the C–X bond in the XCH_2SiH_3 and XCH_2CH_3 molecules are the same, the calculated dipole moment of the SiH_3 group proves to depend on the nature of the halogen atom X.[81]

According to NMR data, the ^{29}Si atom in chloromethyltrimethylsilane is less shielded than in tetramethylsilane, which is consistent with the -I effect of the $ClCH_2$ group[82]. However, if electron-accepting substituents Y (Y = F, Cl, OR, or OCOR) are linked to the silicon atom instead of the methyl groups, the shielding of the silicon atom in compounds of the $ClCH_2SiY_n(CH_3)_{3-n}$ series proves to be greater than in the corresponding $Y_nSi(CH_3)_{4-n}$ molecules[82,83]. One of the possible explanations of the anomalous influence of the chloromethyl group on the shielding of the silicon atom in these compounds is the increase of its $(p-d)_\pi$ conjugation with the heteroatom of the substituent Y under the influence of the electron-accepting chloromethyl group[83].

According to ^1H NMR data[84], the substituents SiX_3 in molecules of the $ClCH_2SiX_3$ series influence the hydrogen atoms of the $ClCH_2$ group only via the inductive mechanism. This conclusion was reached on the basis of the ratio of the coefficients ($\rho/\rho' = 2.7$) in the correlation equations $\delta(CH_2Cl) = \delta_0 + \rho\sigma^*(SiX_3)$ for molecules of the $ClCH_2SiX_3$ (four compounds) and $ClCH_2CH_2SiX_3$ (two compounds) series, which is equal to the coefficient of the decay of the inductive influence of the substituents via the methylene group. However, it is quite evident that the small amount of experimental data makes these conclusions illegitimate.

The ^{19}F NMR spectra show that the electron density at the fluorine atom in the compounds $FCH_2Si(CH_3)_3$ is higher than in the isostructural molecules $FCH_2C(CH_3)_3$ and members of the $F(CH_2)_nSiR_3$ (R = CH_3, C_2H_5, OC_2H_5, or Cl; $n > 1$) series. These data are inconsistent with the existence of the α-effect in the fluoromethyltrimethylsilane molecule and are consistent only with the manifestation of a strong *+I* effect of the $CH_2Si(CH_3)_3$ group[85]. On the other hand, the order in which the ^{19}F NMR chemical shifts of compounds of the $Cl_nCH_{3-n}SiF_3$ series change as *n* is varied is the opposite of that expected on the basis of the inductive effect of the chlorine atoms, which has been explained by the *+M* effect of the latter[86].

The occurrence of two stretching vibration frequencies of the Si–H bond in the infrared spectra of the compounds $ClCH_2SiHRR'$ (in heptane) has been explained by the presence in solution of both molecules with intramolecular coordination between the unshared electron pair of the chlorine atom and the vacant *d* orbital of the silicon atom [the low-frequency ν(Si–H) band belongs to them] and molecules without such coordination[87]. Judging from the splitting of the ν(Si–H) line in the infrared spectra of compounds of the type $ClCH_2SiR_3$, the α-effect weakens with enhancement of the electron-accepting properties of the substituents R.[87] The steric influence of the substituents R affects to some extent the magnitude of the α-effect. The state of aggregation and the nature of the solvent also influence significantly the α-effect. It is a maximum in the gaseous state of the substance and is a minimum in the liquid state owing to its competition with the intermolecular interaction involving the vacant *3d* orbitals of the silicon atom[87].

Two bands are observed in the infrared spectra of gaseous $ClCH_2SiH(CH_3)_2$ and $BrCH_2SiH(CH_3)_2$ as well as their solutions in polar and non-polar solvents[88]. However, in this case the presence of two ν(Si–H) frequencies was explained by the existence of two rotational isomers (formed by the rotation of the $ClCH_2$ group about the Si–C bond) in which the dipole–dipole and steric interaction differ somewhat[88].

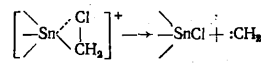
The authors own and the available literature data for the infrared and NMR spectra as well as the dipole moments of compounds of the X_3SiCH_2Y (Y = halogen) series have been analysed[89]. It was concluded that these data are consistent with an intramolecular interaction between the halogen and silicon atoms (α-effect) in halogenomethylsilanes.

It has been shown[90] that the relative basicity of the oxygen atom in the compounds $XX'X''SiOC_2H_5$, determined from the shift Δν(OH) of the stretching vibration frequency of phenol when the latter interacts with these compounds, is correlated with the sum of the Taft inductive constants of the substituents X, X', and X''. However, compounds in which one of the substituents is the chloromethyl group deviate from this correlation owing to the manifestation of the α-effect. The constant $\sigma^* = 0.54-0.57$ of the $ClCH_2$ group, calculated from Δν(OH) by means of a correlation equation, is appreciably lower than the standard value $\sigma^*_{(CH_2Cl)} = 1.05$.[84] Thus the α-effect in molecules of this type can be estimated as amounting to −0.5 of a unit on the scale of the inductive constants σ*.

The ratio of the intensities of the two lines in the ^{35}Cl NQR spectrum of the compound $ClCH_2SnCl_3$ due to the chlorine atoms in the $SnCl_3$ group is 1 : 2 and their splitting (~6%) greatly exceeds the limiting crystal [field?] splitting (1.5–2%).[91] The authors[91] attempted to explain such large splitting by the coordination interaction $Cl\overset{\frown}{-}CH_2-Sn\overset{\frown}{<}$, leading to the asymmetrisation of the tin atom, which in its turn induces the non-equivalence of the Sn–Cl bonds. Nor can one rule out the possibility of an intermolecular interaction being responsible for this non-equivalence[91]. Later preference was given to the latter explanation[92]. However, the cryoscopic distribution of the molecular weights of $ClCH_2SnCl_3$ in benzene shows that this compound is not associated[93].

It has been suggested that the intramolecular coordination interaction of the X and Sn atoms in the molecules $XCH_2SnRR'R''$ is shown in those cases where the tin atom is linked to electronegative substituents R, "capable of exciting the vacant orbitals of tin".[94,95] This interaction is weakened by the competing π-complex formation with participation of the tin atom[94]. Thus, with increase of the number *n* of electronegative substituents at the tin atom in the compounds $(ClCH_2)_{4-n}SnCl_n$ ($n = 0-4$) and $(ClCH_2)_n \cdot Sn(CH_3)_{4-n}$ ($n = 1$ or 2), a downfield shift of the proton signal of the $ClCH_2$ group is observed. The magnitude of this shift in benzene is smaller than in CCl_4, which has been explained[94] by the formation of π-complexes of the type $C_6H_6 \rightarrow SnR_4$.[94]

Rearranged fragments formed via the mechanism[94]



have been detected in the mass spectra of compounds of the $ClCH_2SnRR'R''$ series.

The broadening of the lines in the Mössbauer spectrum of the compound $ClCH_2Sn(CH_3)_3$ can be caused by the unresolved quadrupole splitting[95], in agreement with intramolecular interaction between the chlorine and tin atoms in this molecule.

The intramolecular interaction of atoms not linked directly is manifested more strongly in the solid state of a given substance, where the thermal vibrations of the molecules are considerably weakened[93]. In conformity with this, according to gas electron diffraction data and ^{35}Cl NQR spectra (at 77 K), the mutual influence of the atoms in the $ClCH_2$ group of the $ClCH_2SnCl_3$ molecule in the gaseous and solid states is not the same. Thus in the gas phase all the Sn–Cl bonds are equivalent, while the NQR spectrum of solid $ClCH_2SnCl_3$ demonstrates their significant non-equivalence (see above).

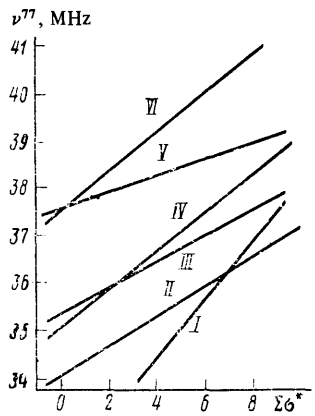


Figure 1. Correlation of the ^{35}Cl NQR frequencies (ν^{77}) of compounds of different series [*I*) $ClCH_2CRR'R''$; *II*) $ClCH_2SiRR'R''$; *III*) $Cl_2CHSiRR'R''$; *IV*) $Cl_2CHCRR'R''$; *V*) $Cl_3CSiRR'R''$; *VI*) $Cl_3CCRR'R''$] with the sum of the Taft inductive constants ($\Sigma\sigma^*$) of the substituents R, R', and R''.

The ^{35}Cl NQR frequencies of compounds of the $ClCH_2ERR'R''$ series with E = Si, Ge, or Sn are higher than for the corresponding organic analogues (E = C) [1–8,96–99] (Fig.1). The points corresponding to the organoelemental compounds $ClCH_2E(CH_3)_3$ lie appreciably above the $\nu^{77} = f(\Sigma\sigma^*_R)$ correlation straight lines plotted for compounds of the ClR and $ClCH_2R$ series[6,100]. Bearing in mind the appreciably greater electronegativity of the carbon atom compared with silicon, germanium, and tin atoms, the opposite ratio of the NQR frequencies of the corresponding organic and organoelemental compounds was to be expected. In the ^{35}Cl NQR spectra of compounds of the $Cl(CH_2)_nERR'R''$ (E = C, $n = 0$, 2, or 3 but not $n = 1$) series the NQR frequency is higher, as expected, than for the corresponding compounds with E = Si, Ge, or Sn. This also applies to the NQR frequencies of compounds of the $ClC \equiv CE(CH_3)_3$ series.

The anomalously high ^{35}Cl NQR frequencies of compounds of the $ClCH_2ERR'R''$ (E = Si, Ge, or Sn) series compared with organic analogues (E = C) are due to the intramolecular interaction between the Cl and E atoms, which we call the α-effect[1–8,96–99]. The possibility of the interaction between the chlorine atoms involved in the C–Cl bond and the silicon atom is also confirmed by a comparison of the relations between the NQR frequencies of these chlorine atoms and their number *n* in molecules of the $Cl_3CC^{35}Cl_nH_{3-n}$ and $Cl_3SiC^{35}Cl_nH_{3-n}$ series (Fig.2). Evidently, as a consequence of this interaction, the increase of the NQR frequencies with increasing number *n* in the spectra of the organosilicon compounds is much smaller than for their carbon analogues (the slope of the correlation straight line II in Fig.2 is smaller than that of line I). The replacement of the CCl_3 group in the $Cl_3CCCl_nH_{3-n}$ molecules by $SiCl_3$ leads to a significant alteration of the mutual influence of the atoms in the $Cl_n.CH_{3-n}$ group. As the chlorine atoms accumulate in this group, each becomes a weaker electron acceptor for E = Si than in the corresponding organic molecules (E = C).[101]

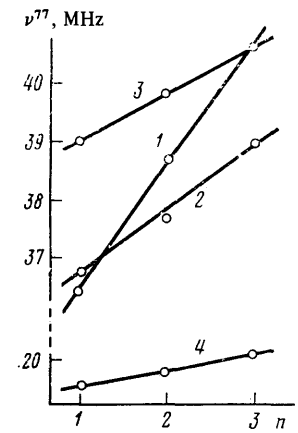


Figure 2. Relation between the ^{35}Cl NQR frequencies (ν^{77}) of compounds of the $Cl_3ECCl_nH_{3-n}$ (E = C or Si) series and the number of chlorine atoms *n*: *1*) for the chlorine atoms in the CCl_nH_{3-n} group with E = C; *2*) for the chlorine atoms in the same group with E = Si; *3*) for the chlorine atoms in the Cl_3C group; *4*) for the chlorine atoms in the Cl_3Si group.

The NQR frequencies of the chlorine atoms linked to silicon in compounds of the $Cl_3SiCCl_nH_{3-n}$ series are satisfactorily consistent with the general relation between the NQR frequencies of compounds of the Cl_2SiRR' series and the sum of the σ* constants of the substituents R. The suggested interaction between the Si atoms and the Cl atoms of the CCl_nH_{3-n} group in the $Cl_3SiCCl_nH_{3-n}$ molecules is shown only by a decrease of the sensitivity of the chlorine atoms of the Cl_3Si group to a change in the number of *n* compared with the organic analogues $Cl_3CCCl_nH_{3-n}$ (the slope of straight line IV in Fig.2 is smaller than that of line III).[101]

Analysis of the ^{35}Cl NQR frequencies of compounds of the $Cl_nCH_{3-n}SiRR'R''$ and $Cl_nCR_{3-n}SiRR'R''$ series as well as the compound $Cl(CH_3)_2SiSi(CH_3)_2Cl$ led[102] to the conclusion that the α-effect is possible only in molecules where the Cl and Si

atoms are separated by the CH_2 or $Si(CH_3)_2$ groups, because only in these cases are the NQR frequencies of the organosilicon compounds higher than those of the corresponding organic derivatives. In reality this conclusion is incorrect.

Further study of the ^{35}Cl NQR spectra of compounds of the $ClCH_2SiRR'R''$, $Cl_2CHSiRR'R''$, and $Cl_3CSiRR'R''$ series showed[5,98,99] that the ratio of the NQR frequencies in the spectra of organic and organosilicon compounds of this type is not always anomalous. For example, the $ClCH_2SiF_3$ frequency is appreciably lower than that of $ClCH_2CF_3$, as was to be expected from the ratio of the electronegativities of the C and Si atoms. The NQR frequencies of compounds of these series are satisfactorily correlated with the sum of the σ^* constants of the substituents R, R', and R'' (Fig.1). For $\Sigma\sigma^* < 7.04$, the NQR frequencies of the organosilicon compounds $ClCH_2SiRR'R''$ are higher than for the corresponding organic analogues $ClCH_2CRR'R''$, i.e. an anomalous ratio of their NQR frequencies is observed. On the other hand, for $\Sigma\sigma^* > 7.04$, the NQR frequencies of the organosilicon compounds are lower than those of the organic derivatives. This is consistent with the ratio of the electronegativities of the Si and C atoms and the inductive effect of the substituents incorporating them. The value of $\Sigma\sigma^*$ for which the ratio of the ^{35}Cl NQR frequencies of the organic and organosilicon compounds $Cl_nCH_{3-n}ERR'R''$ is reversed, decreases sharply with increase of the number of electron-accepting chlorine atoms in molecules of the given series (7.04, 1.67, and 0.25 for $n = 1$, 2, and 3 respectively).

However, the different kinds of ratios of the NQR frequencies of these compounds do not imply that there is no α-effect in the $Cl_nCH_{3-n}SiRR'R''$ molecules for some values of $\Sigma\sigma^*$, while for others the effect does exist. The mechanism of the interaction of atoms in these series of compounds must be the same for all R, because there is a satisfactory linear correlation between their ^{35}Cl NQR frequencies and the sum of the inductive constants σ^* of the substituents. These data show that the α-effect occurs in all molecules containing the $Cl-\overset{|}{\underset{|}{C}}-E$ (or $X-\overset{|}{\underset{|}{C}}-E$) group. However, its manifestation depends on the nature of the substituents linked to the atoms E and C and also on the ratio of the abilities to transmit their electronic influence in organic and organoelemental molecules. Thus the unequal manifestations of the α-effect in the organosilicon compounds $Cl_nCH_{3-n}SiRR'R''$ for different n, R, R', and R'' is caused by their appreciably lower ability to transmit the electronic influence of substituents to the chlorine atom compared with their organic analogues. The ^{35}Cl NQR frequencies of compounds of the $ClCH_2ERR'R''$ (E = Ge or Sn) series are higher than for the corresponding organic derivatives (E = C), because the abilities of these compounds (E = C, Ge, or Sn) to transmit the electronic influence of substituents to the chlorine atom are similar in magnitude (the coefficients ρ in the correlation equation $\nu^{77} = \nu_0 + \rho\Sigma\sigma^*$ are 0.58, 0.43, and 0.46 for E = C, Ge, and Sn respectively[5,99]).

Data concerning the occurrence of an intramolecular noninductive interaction in molecules containing the $X-\overset{|}{\underset{|}{C}}-E$ group (E = Si, Ge, or Sn and X = N, O, or S), obtained by infrared spectroscopy, are extremely contradictory. The nature of the variation of the basicity of the oxygen atom in molecules of the $CH_3O(CH_2)_nSi(CH_3)_3$ [103] and $CH_3O(CH_2)_nC(CH_3)_3$ series with n is the same—the basicity diminishes with increasing n.[103] The increased basicity of the oxygen atom in organic and organosilicon compounds with $n = 2$ has been explained by the effect of hyperconjugation. For compounds of the type $CH_3O(CH_2)_n \cdot Si(CH_3)_3$, the increase of basicity observed on passing from $n = 0$ to $n = 1$ and 3 is consistent with the inductive influence of the trimethylsilyl group. The basicity of the oxygen atom in the $CH_3O(CH_2)_nSiX_3$ (X = H or Cl) molecules proves to be a minimum for $n = 1$, which has been accounted for by the interaction of the oxygen and silicon atoms[103,104]. The smaller basicity of the oxygen atom in $CH_3OCH_2Si(CH_3)_3$ compared with the carbon analogue has also been explained in the same way[105]. Such interaction is manifested most effectively when there are electron-accepting chlorine atoms at the silicon atom[103].

The experimental basicity of the oxygen atom in the $[(CH_3)_3SiCH_2]_2O$ molecules proved to be smaller than was to be expected from the electron-donating properties of the trimethylsilyl group; this is caused by the superposition of the α-effect. Comparison of the basicities of the oxygen atoms shows that the α-effect in $CH_3CH_2OCH_2Si(CH_3)_3$ is stronger than in $[(CH_3)_3SiCH_2]_2O$.[106]

The lower stretching vibration frequency $\nu(C-O)$ in the infrared spectra of the compounds $XO(CH_2)_nSiR_3$ with $n = 1$ compared with their homologues ($n = 2$ or 3) and also with their organic analogues $XOCH_2CR_3$ (X = H, alkyl, or $COCH_3$) is evidently caused by the intramolecular interaction between the oxygen and silicon atoms[107].

On passing from $n = 1$ to $n = 2$ and 3, the basicity of the oxygen atom in compounds of the $(CH_3)_3Si(CH_2)_nOSi(CH_3)_3$ series diminishes. For $n = 2$ and 3, it is virtually the same and close to the basicity in $(CH_3)_3C(CH_2)_nOSi(CH_3)_3$, while for $n = 1$ it is somewhat lower than might have been expected from the electron-donating properties of the trimethylsilyl group. The latter has been explained[108] by an interaction of the type $-O-CH_2-Si$. According to other data[109] the basicity of the oxygen atom in $(CH_3)_3SiCH_2OSi(CH_3)_3$ is consistent with the inductive influence of the $(CH_3)_3SiCH_2$ group ($\sigma^* = -0.26$).

The interpretation of the infrared spectra of compounds of the $ROCOCH_3$ series and of their temperature variation led to the conclusion that the electron-donating capacity of the $R = X_3SiCH_2$ groups is reduced due to the α-effect. This effect leads to a deviation of the frequencies $\nu(C=O)$ and $\nu(C-O-C)$ for $(CH_3)_3SiCH_2OCOCH_3$ from the linear correlation of these quantities with the inductive constants σ^* of the substituents R in compounds of the $ROCOCH_3$ series and to a decrease of the frequencies $\nu(C-O-C)$ for the compounds $H_3COCOCH_2E(CH_3)_2R$ (R = CH_3, C_2H_5, or C_6H_5; E = Si or Ge) compared with $H_3COCO(CH_2)_nE(CH_3)_3$ for $n > 1$ or with $H_3COCO(CH_2)_nR$ [R = $(CH_3)_3C$ or CH_3; $n = 1-4$].[110] The acetoxy-group in compounds of the $H_3COCOCH_2Si(CH_3)_{3-n}R_n$ (R = OC_2H_5 or $OCOCH_3$) series increases the shielding of the silicon atom compared with the compounds $R_nSi(CH_3)_{4-n}$. On the other hand, according to its inductive effect, deshielding of the silicon atom would have been expected[111].

The basicity of the oxygen atom in the $H_3COCH_2EH_3$ (E = Si or Ge) molecules is lower than in the carbon analogue (E = C), which is inconsistent with the electron-donating properties of the EH_3 groups for E = Si or Ge and has been explained[112,113] by the $(p-d)_\pi$ interaction between O and E (E = Si or Ge) atoms separated by the CH_2 group.

The frequencies $\nu(C-O-R)$ and $\nu(OH)$ in the infrared spectra of the compounds $RO(CH_2)_nGe(CH_3)_3$ [R = H or $Si(CH_3)_3$; $n = 1-4$] for $n = 1$ are lower than for $n = 2-4$ and are also lower than for the carbon analogues $RO(CH_2)_n \cdot C(CH_3)_3$. This has been explained by the lability of the C–O bond caused by the α-effect. The relative basicities of the oxygen atom in molecules of the $(CH_3)_3E(CH_2)_n \cdot OSi(CH_3)_3$ (E = C or Ge; $n = 1-4$) series are consistent

with the electron-donating properties of the $(CH_2)_nGe(CH_3)_3$ groups. For $n=1$ and 2, the basicity is higher than for $n=3$ and 4.[114]

The relative basicities of the alcohols HOR, determined from the shift of the stretching vibration frequency ν(OH) of phenol, are correlated with the inductive constants σ^* of the substituents R. The basicities of the compounds $HO(CH_2)_nSi(CH_3)_3$ with $n=1$ and 2 also obey this correlation. The relative acidities of the latter likewise obey a linear correlation between the acidity of the alcohols HOR [determined from the shift of ν(OH) in the infrared spectra of their mixtures with tetrahydrofuran] and the σ^* constants of the substituents R. These data are inconsistent with an interaction between the silicon and oxygen atoms in organosilicon compounds containing the $-O-\overset{|}{C}-Si<$ group[115].

The ^{29}Si NMR chemical shifts of compounds of the $ROSi(CH_3)_3$ series are correlated with the inductive constants σ^* of the substituents R. Compounds with $R=CH_2Cl$ and $CH_2Si(CH_3)_3$ do not obey this correlation. The ^{29}Si NMR data show that the $CH_2Si(CH_3)_3$ group has a weaker electron-accepting activity when it is linked to an oxygen atom. The constant $\sigma^*[CH_2Si(CH_3)_3]$, calculated[109] from the correlation equation on the basis of the experimental quantity δ(Si) in the $(CH_3)_3SiCH_2OSi(CH_3)_3$ spectrum, is 0.15 ± 0.05.

The acidity of alcohols of the $HO(CH_2)_nSi(C_6H_5)_3$ series increases on passing from $n=1$ to $n=2$, the increase being particularly pronounced for $n=0$. The acidity of isostructural organogermanium alcohols $HO(CH_2)_nGe(C_6H_5)_3$ increases on passing from $n=2$ to $n=1$ and further to $n=0$. This sequence in the variation of the acidities of organoelemental alcohols is inconsistent with the electron-donating inductive effects of the triphenylsilyl and triphenylgermyl groups and can be explained by the $(p-d)_\pi$ interaction between the oxygen atom and the silicon or germanium atom via the methylene group. It has been suggested that such interaction is responsible also for the decrease of acidity on passing from E = Ge to E = Si and further to E = C in molecules of the $HOCH_2E(C_6H_5)_3$ series[116].

The basicity of the nitrogen atom in trimethylsilylmethylamine is higher than in its carbon analogue (by a factor of 5.69) or in γ-trimethylsilylpropylamine (by a factor of 1.5),[117] which agrees with the electron-donating effect of the trimethylsilyl group.

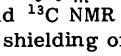
The basicity of compounds of the $H_2N(CH_2)_nSi(OC_2H_5)_m\cdot(CH_3)_{3-m}$ ($m=0-3$) series, determined spectroscopically, is much lower for $n=1$ than for $n=2-4$. This has been explained by the effect of hyperconjugation, which exceeds, when $n=1$, the opposite inductive effect of the silyl group[118].

Compounds of the $H_2N(CH_2)_nSi(OC_2H_5)_m(CH_3)_{3-m}$ series have also been studied by the ^{29}Si, ^{14}N, and ^{13}C NMR methods[119]. The observed increase of the shielding of the silicon atom in these compounds for $n=1$ and 2 relative to compounds of the $H(CH_2)_nSi(OC_2H_5)_m(CH_3)_{3-m}$ series has been explained by the intensification of the $(p-d)_\pi$ interaction between the silicon and oxygen atoms (in the ethoxy-group) under the influence of the electronegative group NH_2. This inductive influence decays for $n\geq3$. It has been suggested that the more pronounced shielding of the nitrogen atom in the aminomethyl derivatives (which is almost independent of the number m) compared with other members of this series ($n\geq2$) is inconsistent with the interaction between the silicon and nitrogen atoms in these molecules[119]. However, on the basis of NMR data, one can hardly draw inferences about this interaction, because the ^{14}N, ^{29}Si, etc. NMR shifts are not direct characteristics of the electron density of the indicator atom. This is evident also from the ^{14}N NMR spectra of compounds of the type $H_2N(CH_2)_n\cdot Si(OC_2H_5)_m(CH_3)_{3-m}$ investigated. For example, a change in the number m for $n=1$ does not affect δ_N and the chemical shift of the ^{14}N NMR signal in the spectrum of aminomethyltriethoxysilane differs by only 1 p.p.m. from δ for methylamine, etc.

The basicity of the amines $H_2C(CH_2)_mN(CH_2)_nSiR_3$ ($m=3-5$) for $n=1$ is lower than for $n=2$,[120-122] which is due to the α-effect in the molecules with $n=1$. The determination of the relative acidities of the hydrogen atom linked to the nitrogen atom in compounds containing the $RNHCH_2Si$ group by infrared spectroscopy[123] showed that they exhibit the α-effect. The magnitude of this effect depends on the nature of the substituent R linked to the nitrogen atom and is a maximum for R = alkyl. For $R=C_6H_5$, the α-effect is reduced owing to competition with p, π conjugation involving the aromatic ring. For $R=CH_3OC(O)$, there is no α-effect[123].

In molecules of the $R_2NCH_2E(CH_3)_3$ series, the basicity of the nitrogen atom for E = Ge is somewhat lower[32] and for E = Sn is lower by 4 orders of magnitude than for E = C.[124] The appreciably reduced basic properties of the nitrogen atom in trialkylaminomethylstannanes have been explained by the increase of the coordination number of the tin atom due to the formation of an intramolecular coordinate bond with the nitrogen atom, i.e. by the transfer of the unshared electron pair of the nitrogen atom to the vacant orbital of the tin atom with partial sp^3d character[124]. The upper limit to the strength of the intramolecular coordinate bond N → Sn ($\Delta\Delta H\cong5.5$ kcal mol^{-1}) was estimated from the decrease of basicity by means of the relations $k_1/k_2=\exp(-\Delta\Delta E/RT)$ and $\Delta\Delta F=\Delta\Delta H-T\Delta\Delta S^0$, neglecting the change in the entropy term[124]. Later[125] the authors admitted that these data and the hypothesis of the intramolecular coordination of the tin and nitrogen atoms based on them are erroneous. They found that the basicity of the amines containing the $>N-\overset{|}{C}-E<$ group increases in the following sequence of different E: C > Ge > Sn > Si.

The intramolecular coordination interaction between nitrogen and tin atoms is indicated by the retardation of the inversion of nitrogen in trialkyl(*N*-aziridinomethyl)stannanes; apart from overcoming the inversion barrier, a change in the configuration of these compounds requires the rupture of the N → Sn bond.[124]

In contrast to tetra-alkylstannanes, the ultraviolet spectra of trialkyl(aminomethyl)stannanes exhibit a slight bathochromic shift and an appreciable increase of the extinction coefficient[124], which is consistent with the N → Sn coordination. The absence of an intermolecular interaction in this case is confirmed, for example, by cryoscopic and electrothermic studies of the compound  .[124,126]

The absence of quadrupole splitting and the small changes in the chemical shifts in the Mössbauer spectra of compounds of the XCH_2SnR_3 (X = H_2N, $R_3\overset{+}{N}$, RO, F, or Cl) series[95,127] are inconsistent with intramolecular coordination in these molecules[95,128]. This may be caused by the inadequate sensitivity of the method[124].

Certain examples of the anomalous influence of the groups ER_3 (E = Si, Ge, or Sn), which are inconsistent with their inductive effect on the atom X in molecules containing the $X-\overset{|}{C}-ER_3$ fragment, have also been quoted in reviews[125-131]. This anomalous influence is usually explained by the interaction between the unshared electron pair of the atom X and the vacant *d* orbitals of the atom E.[129,131].

Thus the results presented below show that data concerning the existence of the α-effect in molecules containing the X–C–E (E = Si, Ge, or Sn) group are at present contradictory. However, one must bear in mind that many theoretical conclusions are insufficiently well-founded. Data derived by certain research methods, on the basis of which the α-effect is accepted or rejected, do not permit inferences concerning the nature of the distribution of electron density at the E and X atoms, because such data are determined by contributions from several uncontrolled factors. This applies primarily to ^{14}N, ^{29}Si, etc. NMR spectra. Furthermore, the contradictory nature of the conclusions concerning the existence of the α-effect is caused by the fact that the nature of its manifestation in molecules containing the X–C–E group depends on the electron-accepting properties of substituents linked to the C and E atoms and also on the ratio of the abilities to transmit the inductive influence of substituents to the atom X in organic (E = C) and organoelemental (E = Si, Ge, or Sn) compounds. These characteristics of the manifestation of the α-effect have usually been disregarded. The conclusions concerning the existence of the α-effect, based on a comparison of the results of studies of individual pairs of organic and organoelemental compounds, cannot therefore be regarded as reliable.

The vast majority of the available experimental data indicate a non-inductive interaction between the atoms X and E in molecules containing the X–C–E group. Systematic study of ^{35}Cl NQR spectra of compounds containing this group (E = C, Si, Ge, or Sn) showed that the α-effect exists in all these molecules but is not manifested in the same way. By analogy with these data and also bearing in mind the results obtained by other research methods, one can assume that the α-effect exists in all molecules containing the X–C–E group.

IV. THE NATURE OF THE α-EFFECT

Views concerning the nature of the α-effect in molecules containing the X–C–E group are contradictory and the majority of them do not have a convincing basis. They are based on the analysis of data obtained in the study of the corresponding compounds by physical methods which are unsuitable for the investigation of the mechanism of the mutual influence of atoms in molecules. The quantum-mechanical calculations carried out on certain molecules to elucidate the nature of the α-effect also failed to solve the problem of the mechanism of this interaction. The anomalous (inconsistent with the inductive effect of the geminal substituent) physical and chemical properties of compounds containing the X–C–E group are usually explained by the coordination interaction between the atoms X and E with transfer of electron density from the atom X to the atom E. The commonest mechanism of this transfer is $(p-d)_\pi$ conjugation of the unshared electron pair of the atom X with the *d* orbitals of the atom E through space[81,112,113,116]. The principal arguments in support of this interaction—the anomalous nature of the properties of these compounds and the possibility, in principle, of the involvement of the unshared electron pairs and vacant *d* orbitals of the corresponding atoms in the formation of chemical bonds—are merely speculative.

If the intramolecular coordination interaction in the group X–C–E does indeed occur, it is to be expected that the ECX angle should be smaller than the tetrahedral value, that the non-bonding E...X distance should approach the sum of the covalent radii of these atoms, and that the E–C and C–X bond lengths should have anomalous values. However, the experimental geometry of the $ClCH_2SiH_3$ molecule[132] does not confirm this hypothesis. The ClCSi angle in this molecule is 109.3°, the Si–C and C–Cl bond length have the "normal" values (1.88 and 1.788 Å respectively), and the distance between the Si and Cl atoms is 3.0 Å, i.e. appreciably greater than the sum of their covalent radii.

According to gas electron diffraction data[93], the $ClCH_2.SnCl_3$ molecule has the structure of a somewhat distorted tetrahedron. All the Sn–Cl bonds have the same "normal" length (2.34 Å), which is less than the sum of the covalent radii (2.39 Å). The Sn–C bond length (2.23 Å) is somewhat greater than the sum of the covalent radii of the tin and carbon atoms (2.17 Å) and the length of the Sn–C bonds in other organic derivatives of tin. The C–Cl bond (1.74 Å) is shorter than in saturated organic compounds and its length is close to that of a C–Cl bond adjoining a double bond, for example in $Cl_2C=CCl_2$ (1.72 Å). The ClCSn angle (113°) is somewhat greater than the tetrahedral value and the non-valent Sn...Cl distance (3.31 Å) is greater than the sum of the covalent radii (2.39 Å) but smaller than the sum of the van der Waals radii (3.95 Å) of tin and chlorine atoms. Although this distance is sufficient for coordination interaction between the Sn and Cl atoms, nevertheless there is no direct evidence for such coordination.

It has been suggested that the characteristics of the changes in the basicity of the oxygen atom in molecules of the $[(CH_3)_3Si(CH_2)_n]_2O$ ($n = 1-4$) series[106] and the low stretching vibration frequencies ν(C–O) and ν(HO) [107] in the compounds $XOCH_2Si(CH_3)_3$ compared with their organic analogues and other members of the $XO(CH_2)_nSi(CH_3)_3$ [X = H or $Si(CH_3)_3$] series are caused by the $(p-d)_\sigma$, $\sigma_{OC} \rightarrow d$, or $\sigma_{OH} \rightarrow d$ interactions[106,107]. The last interaction has also been postulated in the $HOCH_2Ge(CH_3)_3$ molecule[107]. The α-effect in the molecules of acetoxysilanes $H_3COCOCH_2.Si(CH_3)_2X$ has been interpreted as $\sigma_{C(O)-O} \rightarrow d$, $\sigma_{C(O)-O} \rightarrow \sigma^*_{(O)C-Si}$, or $\sigma_{C(Si)-O} \rightarrow d$ interaction[110]. The shielding of the protons of the methylene group $XCH_2Sn\lesssim$ in the molecules $XCH_2Sn(C_2H_5)_2Cl$, which is smaller than expected on the basis of the electronegativity of the tin atom, has been explained by the partial transfer of the σ-electrons of the CH_2–X bond (X = Cl or OCH_3) to the vacant 5*d* orbitals of the tin atom (σ–*d* conjugation).[133]

Analysis of the orbital interactions of the α-carbofunctional silanes XCH_2SiH_3 (X = NH_2, OH, or F) and the corresponding carbon analogues, based on the calculation of the wave functions in terms of the CNDO/2 approximation and the Mulliken analysis of the orbital populations, led to the conclusion that there exist two mechanisms of the electron-accepting influence of the second atom on the geminal heteroatom (two mechanisms of the α-effect)[134,135]: (1) interaction through space between the upper occupied molecular orbitals and low-lying antibonding orbitals ($n - \sigma + \sigma^*$), which

is reflected by the resonance structure $^{+}X-CH_2\ H-SiH_2$; the extent of this interaction diminishes in the following sequence of X: $H_2N > OH > F$; (2) interaction via bonds, which is most marked for X = F.

The sequence of the changes in the calculated (in terms of the CNDO/2 approximation without taking into account the *d* orbitals of the silicon atom) enthalpy of the reversible acid–base interaction ΔH for the compounds $X(CH_2)_nEH_3$ (E = C or Si; X = HO or H_2N; $n = 0-3$) is consistent with the sequence in the variation of the experimental basicities or acidities of these compounds determined in the gas phase. The enthalpy was calculated as the difference between the total energies *E*: $\Delta H = E_{(ROH)} - E_{(RO^-)}$ for the reaction $RO^- + H^+ \rightarrow ROH$ and $\Delta H = E_{(RNH_3^+)} - E_{(RNH_2)}$ for the reaction $RNH_2 + H^+ \rightarrow RNH_3^+$.

The basicity of the amine $H_2NCH_2Si(CH_3)_3$ is lower than for other members of the $H_2N(CH_2)_nSi(CH_3)_3$ series. On the other hand, the basicity of the alcohols $HO(CH_2)_nSi(CH_3)_3$ diminishes successively with increase of *n*. On the basis of the analysis of the orbital interactions, the unequal influences of the $(CH_3)_3Si$ group on the basicity of $H_2NCH_2Si(CH_3)_3$ and $HOCH_2Si(CH_3)_3$ have been explained by the stronger interaction of the unshared electron pair of the nitrogen atom with the Si–C bond compared with the oxygen atom, which leads to a decrease of the energy of the $n-\sigma$ orbital when the latter interacts with the antibonding σ^*_{Si-C} or σ^*_{Si-H} orbital[135]. It has been suggested[134] that the α-effect is a consequence of the high polarisability of the silicon atom, which is responsible for the existence of low-lying antibonding orbitals.

The inclusion of the vacant *d* orbitals of the silicon atom in the calculation on the XCH_2SiH_3 molecules reduces somewhat the total energy of these molecules and the energies of the individual orbitals. However, this does not alter qualitatively the tendency towards a distribution of the charges on the silicon atom and particularly on the heteroatoms of the substituents X when the latter are varied[134]. An analogous conclusion had been reached earlier[136] on the basis of *ab initio* non-empirical calculations with a contracted Gaussian basis. Furthermore, the contribution of the antibonding orbital σ^*_{Si-H} to the energy of a low-lying vacant molecular orbital is much greater than the contribution of the *d* orbitals[134].

The problem of the involvement of the vacant *d* orbitals of the atoms of non-transition elements in the formation of chemical bonds has attracted the attention of many investigators for a long time. Numerous quantum-mechanical calculations, including non-empirical calculations, have been carried out for its solution. The view (based on these calculations) that the presence of vacant *d* orbitals in the valence shells of atoms of non-transition elements hardly influences the properties of compounds incorporating them, because these orbitals are energetically so unfavourable and so diffuse that they are incapable of interacting in any way appreciably with the other valence orbitals, is nowadays gaining increasing currency (see, for example, Bochvar et al.[137] and Korol'kov[138]). In this connection it is evident that the α-effect can also be accounted for without taking into account the contribution of the vacant *d* orbitals of the atom E (E = Si, Ge, or Sn).

The α-effect in compounds containing the $X-\overset{|}{\underset{|}{C}}-E$ group is caused by the interaction of quite definite orbitals of the atoms E and X (see above). The occurrence of this non-inductive interaction between atoms and its nature can be established only with the aid of physical methods whereby one can follow the populations of these particular orbitals. One of these few methods is nuclear quadrupole resonance, which yields information about the spatial distribution of the electron density of the indicator atom. Other physical methods used to investigate the α-effect (see above) do not provide such information. The results of quantum-mechanical calculations also do not permit the elucidation of the nature of the α-effect.

According to ^{35}Cl NQR spectroscopic data for compounds of the $ClCH_2ERR'R''$ (E = C, Si, Ge, or Sn) series, the p_σ electrons of the chlorine atom, i.e. the electrons of the C–Cl bond, are involved in the interaction with the E atom of these molecules[1-8,97,139]. This follows from the higher ^{35}Cl NQR frequencies of the organoelemental compounds (E = Si, Ge, or Sn) compared with organic analogues (E = C) (see the previous Section).

The NQR frequency ν or the quadrupole coupling constant of the molecule e^2Qq are related to the number of unbalanced electrons of the chlorine atom V_p as follows (see, for example, Refs.92, 140–142):

$$e^2Qq_{mol} = e^2Qq_0 \cdot V_p = e^2Qq_0\left(\frac{N_x + N_y}{2} - N_z\right),$$

where e^2Qq_0 is the atomic quadrupole coupling constant and N_x, N_y, and N_z are the populations of the p_x, p_y, and p_z orbitals of the chlorine atom. Hence it is seen that the quantity e^2Qq can increase either with decrease of the population of the chlorine p_σ orbital (p_z orbital), involved in the formation of the C–Cl bond, or with increase of the population of the orbitals of its unshared electron pairs (p_x or p_y orbitals). The hypothesis that the populations of the $3p_x$ and $3p_y$ orbitals of the chlorine atom in organoelemental molecules are higher than in the isostructural organic molecules, where the populations of the p_x and p_y orbitals are virtually equal to 2, is unrealistic. Therefore the increase of the ^{35}Cl NQR frequency for compounds of the $ClCH_2ERR'R''$ series having E = Si, Ge, or Sn compared with organic analogues (E = C) as well as other anomalous properties of the compounds containing the $Cl-\overset{|}{\underset{|}{C}}-E$ or $X-\overset{|}{\underset{|}{C}}-E$ (E = Si, Ge, or Sn) group are caused by the decrease of the population of the p_σ orbital of the chlorine (or X) atom, i.e. by the involvement in the interaction with the E atom of the electrons of the C–Cl (C–X) bond[1-8,97,139]. This is an experimentally established fact. The participation of the p_σ electrons of the chlorine atom in this interaction is also confirmed by the comparatively low parameter of the asymmetry of the electric field gradient η at the location of the atomic nucleus of chlorine in chloromethylsilane $ClCH_2SiH_3$ ($\eta = 0.048$), which is close to the asymmetry parameter for $ClCH_2CH_3$ ($\eta = 0.035$). Consequently the hypothesis of the coordination interaction between the E and X atoms in the $X-\overset{|}{\underset{|}{C}}-E$ group with participation of the unshared electron pair of the X atom has not been confirmed experimentally.

One can only speculate in what way the E atom is involved in this interaction. According to the generally accepted view, the atoms E = Si, Ge, or Sn possess electron-accepting properties by virtue of their vacant *d* orbitals (see, for example, Refs.23, 131, 143, and 144). On this basis, one can assume that the p_σ electrons of the C–Cl (C–X) bond pass to the vacant *d* orbitals of the E atom and an electron-deficient three-centre bond is therefore formed between the

E, C, and Cl atoms[1-3]. The possibility of the formation of a three-centre bond as a result of the sharing of a single electron pair by three atomic nuclei was pointed out a long time ago by Longuett–Higgins[145]. The presence of such hypervalent bonds has been postulated in diborane[145-148], carbaboranes[149], etc. (see, for example, Refs,147, 148, and 150), but the existence of such bonds has not so far been confirmed experimentally.

In molecules containing the X–C–E group the C–X bond can also be polarised under the influence of the E atom, which should lead to a decrease of the p_σ electron density of the X atom[3]. This model of the intramolecular interaction does not conflict with the steric structure of molecules of the XCH_2ER_3 series established by gas electron diffraction[93] and microwave spectroscopy[132], since it does not require a decrease of the XCE angle relative to the tetrahedral value[2,3].

Analysis of the experimental data established a unique anomalous relation between the ^{35}Cl NQR frequencies of all compounds containing the Cl–C–E group and the charge (or, to a first approximation, the electronegativity) of the E atom[1-5]: with increase of the electronegativity (negative charge) of the E atom, the NQR frequencies of such compounds diminish (the p_σ-electron of the chlorine atom increases) and, conversely, with decrease of the electronegativity of the E atom, the NQR frequencies increase (the p_σ-electron density of the chlorine atom diminishes). Compounds with an E atom having unshared electron pairs (E = N, O, F, etc.), vacant *d* orbitals (E = Si, Ge, Sn, etc.), as well as atoms lacking either feature (E = H or C) obey this relation. The relation has been confirmed by the correlation analysis of the ^{35}Cl NQR frequencies of, for example, compounds of the $ClCH_2E^nR_{n-1}$ (*n* is the valence of the E atom) series[4]. The NQR frequencies of compounds of the $ClCH_2CR_3$ series are correlated with the inductive constants σ^* of the substituent CR_3. For $E \neq C$, such a correlation does not hold. The deviations of the NQR frequencies $\Delta\nu$ of compounds with $E \neq C$ from the above correlation are in their turn satisfactorily correlated with the electronegativity of the E atom (according to Pauling). The last correlation is obeyed by the deviations $\Delta\nu$ both for compounds with an E atom having unshared electron pairs or vacant *d* orbitals and for compounds with E = H as well as the average value of $\Delta\nu$ ($\Delta\nu_{av} = 0$) for compounds with $E^nR_{n-1} = CR_3$.

An analogous anomalous relation is shown also in the case of other physical and chemical methods for the investigation of compounds containing the X–C–E group. The anomalous properties of all these compounds (whatever the E) are due to the interaction of the E atom with the electron cloud of the C–X (C–Cl) bond, which follows from their ^{35}Cl NQR spectra. Bearing this in mind as well as the general anomalous dependence of the distribution of electron density at the X atom in the X–C–E group on the nature of the E atom, one can assume that the anomalous relation is caused by the same mechanism of the interaction of the X and E atoms whatever the E. This general mechanism can involve the electrostatic interaction of the charge of the E atom, directly through the field, with the electron cloud of the C–Cl (C–X) bond, because this interaction is almost independent of the presence of unshared electron pairs or vacant *d* orbitals in the E atom[2,4,5,139,153]. Furthermore, the electrostatic mechanism of the geminal interaction is indicated by the finding that virtually all interactions in the molecules are in fact electrostatic, the E atom influences all the C–X bonds in the given molecule in the geminal position with respect to it to virtually the same extent, etc.[5,153] The interaction of the E and Cl atoms in these molecules directly through the field has been confirmed by the ^{35}Cl NQR spectra of compounds of the $Cl_nCH_{3-n}CHClOR$ series[154,155], in which the resonance frequency of the β-chlorine atom corresponds to the inductive influence of the OR group on the latter, while the frequency of the α-atom is anomalously low. The interaction of the α- and β-chlorine atoms with the oxygen atom along the chemical bonds, the nature of the changes in their NQR frequencies would be the same. In the linear molecules Cl–C ≡ E the intramolecular interaction of the geminal Cl and E atoms takes place only along chemical bonds. The E atoms therefore influence the NQR frequency (or the quadrupole coupling constant) of these compounds in conformity with the inductive effect of the E atoms or the substituents incorporating them[4,5,139,153].

The calculated contribution $\Delta\nu$ to the ^{35}Cl NQR frequency of the interaction of the charge of the E atom with the electron cloud of the C–Cl bond directly through the field for certain molecules of the $ClCH_2E$ series agrees well with the experimental data and the quantum-chemical calculation of the charges on the E atoms in these molecules[156-158]. For example, the quantity $\Delta\nu = 4.2$–6.3 MHz (for different amounts of ionic character of the C–Cl bond, for different charges on the oxygen atom calculated for different parametrisations in terms of the CNDO approximation taking into account the error of the experimental determination of the Stark shift used in the calculation, etc.), calculated for the chloromethyl ether $ClCH_2OCH_3$, agrees satisfactorily with the deviation of the experimental NQR frequency of this ether from the linear correlation between the ^{35}Cl NQR frequencies of compounds of the $ClCH_2CR_3$ series and the inductive constants σ^* of the substituents CR_3 ($\Delta\nu_E = 4.9$ MHz). For $ClCH_2Si(CH_3)_3$, the quantities $\Delta\nu$ and $\Delta\nu_E$ are respectively 3.72 and 3.56 or 2.50 MHz, etc.[157]

The ^{35}CL NQR frequencies of compounds containing the Cl–Z–E and Cl–Z–E groups (Z = C, Si, Ge, P, etc.) obey the anomalous relation which holds for compounds containing the Cl–C–E group[2,4,5,98,139,153,159,160]. The contribution $\Delta\nu$ of the geminal interaction between the Cl and E atoms in the molecules ClZ(OR)XX′ (Z = C, Si, or Ge) is inversely related to the bulk of the central atom Z, i.e. to the distance between the E = O atom and the centre of the electron cloud of the Z–Cl bond[159]. An analogous relation has been observed also for compounds of the ClZ(OR)X series with Z = P or As.[159]. These data are also in good agreement with the electrostatic mechanism of the interaction of the Cl and E atoms in molecules containing the Cl–C–E (X–C–E) group and therefore with the electrostatic mechanism of the α-effect, which is a special case (for E = Si, Ge, Sn, etc.) of the general electrostatic effect of the geminal interaction.

The above data, obtained in the study by physical and chemical methods of compounds of Group IVB elements containing the X–C–E fragment (E = Si, Ge, or Sn; X = halogen, O, N, or S), show that in the vast majority of

cases the E atoms influence the substituent X not in conformity with the electronegativity of the E atom and the inductive effect of the group incorporating it. This non-inductive interaction of the X and E atoms has been called the α-effect. There exist most contradictory views concerning the existence of the α-effect and its nature. However, systematic studies of the ^{35}Cl NQR spectra of organosilicon compounds containing the Cl–C–Si group have shown that the α-effect occurs in all molecules of this type and that the conflicting conclusions concerning its existence arose from the fact that they were usually based on a comparison of data obtained in the study by some method of individual pairs of isostructural organoelemental and organic compounds or short series of compounds.

On the other hand, the nature of the manifestation of the α-effect depends significantly on the electron-accepting properties of the substituents linked to the C and E atoms and on the ability to transmit the inductive influence of the substituents to the indicator E atom in organic and organoelemental compounds and on the research technique employed, which may not reflect adequately the nature of the distribution of the electron density at the E and X atoms. The nature of the α-effect is usually inferred solely on the basis of the postulated possibility, in principle, that specific orbitals of the E and X atoms are involved in the formation of chemical bonds, without any experimental evidence for this hypothesis. Quantum-mechanical calculations also fail to provide a convincing explanation of the α-effect.

The ^{35}Cl NQR spectra of compounds containing the Cl–C–E group (E = C, Si, Ge, or Sn) indicate unambiguously the involvement of the p_σ electrons of the chlorine atom (the electrons of the C–Cl bond) in the interaction with the E atom. Systematic study of the ^{35}Cl NQR spectra of compounds of this type, in which the E atom has unshared electron pairs, vacant *d* orbitals, or neither one nor the other showed that their anomalous properties are caused by the electrostatic interaction directly through the field due to the charge of the E atom with the electron cloud of the C–Cl (C–X) bond, i.e. by the polarisation of the C–Cl (C–X) bond under the influence of the electric field generated by the charge of the E atom, and not by the coordination interaction between the E and Cl (or X) atoms, presupposing the transfer of electron density from the X atom to the E atom. The α-effect is only a special case of such electrostatic interaction. It is quite natural that the charge of the X atom interacts in the same way with the electron cloud of the C–E bond.

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Adamantane Structures in the Chemistry of Silicon, Germanium, and Tin

V.F.Mironov, T.K.Gar, N.S.Fedotov, and G.E.Evert

The methods of synthesis and properties of compounds with the adamantane structure containing silicon, germanium, or tin atoms in the side chain or substituting carbon atoms in the adamantane lattice are examined. The review includes studies published towards the beginning of 1979.
The bibliography comprises 177 references.

CONTENTS

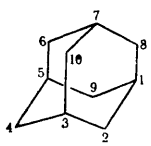
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I. INTRODUCTION

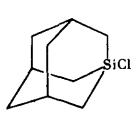
Adamantane, its analogues, and their derivatives are known to have unique physicochemical properties[1-13]. Studies designed to synthesise adamantane structures with Group IVB elements, particularly silicon, have begun to develop recently; a new field has been established in the chemistry of Group IVB elements to which more than 170 original publications have already been devoted.

Compounds of Group IVB elements having a three-dimensional skeleton comprising any atoms with the same configuration as the skeleton of carbon atoms in adamantane, which can be regarded as the unit cell of the three-dimensional carbon network in diamond, can be divided into two large classes. The first class includes compounds in which the atom of the Group IVB element is not incorporated in the adamantane skeleton. Such compounds can be called respectively silyl-, germyl-, stannyl-, and plumbyl-adamantanes. The second class includes compounds in which the atom of the Group IVB element is incorporated in the adamantane skeleton, i.e. substitutes a carbon atom. Such compounds can be called respectively sila-, germa-, stanna-, and plumba-adamantanes.

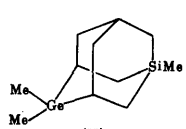
The following numbering has been adopted for the carbon skeleton of adamantane:



Regardless of the number of substituents, this skeleton is designated by the symbol Ad. If one or more carbon atoms in the adamantane skeleton have been substituted by atoms of other elements, then the principle of the "oxa-aza" nomenclature is used in naming such compounds. For example, compounds (I) and (II) are called respectively 1 chloro-1-sila-adamantane, and 1,4,4-trimethyl-1-sila-4-germa-adamantane:



(I)



(II)

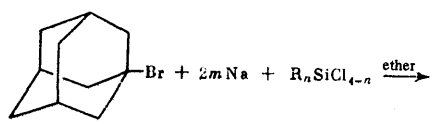
Alphabetic symbols for such structures have not as yet been proposed, since these compounds have in most cases not been synthesised or are represented by single specimens. However, for 1,3,5,7-tetrasila-adamantanes, i.e. compounds having the skeleton of the unit cell of carborundum and frequently called carborundanes, it is reasonable to introduce a designation, since this class is already represented by numerous compounds and is nowadays widely investigated. Without taking into account the substituents, the unit cell of carborundum is designated by the symbol Cb.

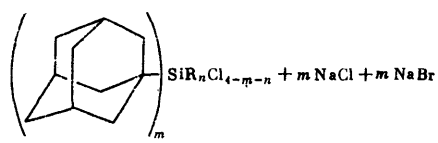
II. SILYLADAMANTANES

This class includes compounds having the structure AdSi$\equiv$ or AdRSi$\equiv$, where R can be any group of atoms or any element.

1. Methods of Synthesis

Silyladamantanes with the adamantyl group linked directly to the silicon atom have been recently obtained by the Wurtz reaction independently by several groups of investigators. No and coworkers[14-18] have studied this reaction most widely:

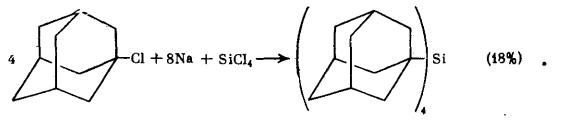




R = Et, n-Pr, n-Bu, Ph, or Me; $n = 1-3$, $m = 1-3$.

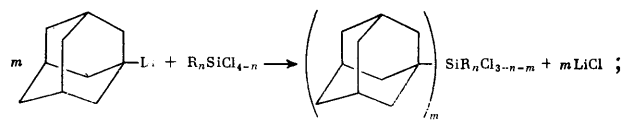
According to the authors, the reaction proceeds with high yields (50–80%) of the required products, although it is accompanied by the formation of diadamantane. The authors note that it is possible to replace only one chlorine atom in chlorosilane by the adamantyl group.

However, Roberts[19] was able to obtain tetra-adamantylsilane by the Wurtz reaction (in a low yield):



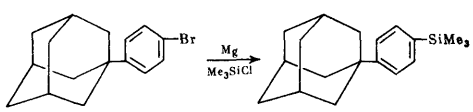
Mironov et al.[20] also investigated the synthesis of silyladamantanes using sodium and lithium, but they were able to obtain 1-trimethylsilyladamantane only in a very low yield. Roberts[19] likewise notes that trimethylsilyladamantane cannot be synthesised by the Wurtz reaction. The reported synthesis[14] of trimethylsilyladamantane by the Wurtz reaction (in 70% yield) must be regarded as erroneous. The authors of these studies claim that the melting point of their compound is 236 °C, while the true melting point of trimethylsilyladamantane proved to be ~35 °C.[21]

1-Adamantylalkyl(aryl)chlorosilanes can also be obtained from lithioadamantane[14]:

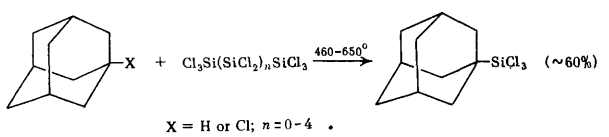


The reaction takes place readily; the main difficulty of the method consists in the multistage synthesis of the initial lithioadamantane, which is ultimately responsible for the very low yields of the desired adamantylalkyl(aryl)chlorosilanes.

The analogous synthesis via organomagnesium compounds has not so far been used, although the possibility of preparing a Grignard reagent from 1-bromoadamantane (in 60% yield) has been reported[22]. However, the synthesis of a compound of the type AdRHal via organomagnesium compounds has proved possible[23]:



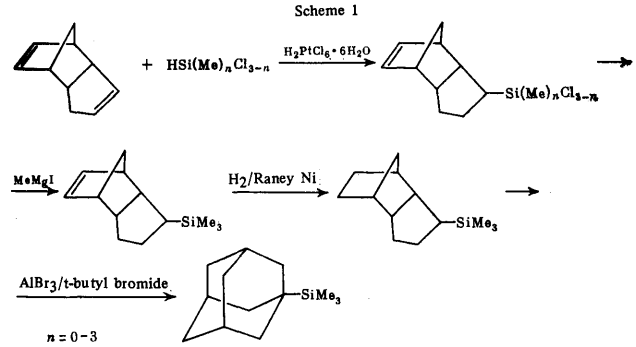
The use of organosodium synthesis has not yet permitted the preparation of trichlorosilyladamantane. This compound has been synthesised[21,24,25] by passing adamantane or chloroadamantane mixed with hexachlorodisilane or perchloropolysilanes through a quartz tube heated to 450–650 °C.



The reaction is carried out at atmospheric pressure and probably proceeds via a carbenoid mechanism, which involves the insertion of the $SiCl_2$ group in the C–Cl bond of chloroadamantane.

Yet another interesting method of synthesising trimethylsilyladamantane, in which the cyclopentadiene dimer and hydrochlorosilanes are used as the starting materials has been outlined recently[26] (Scheme 1).

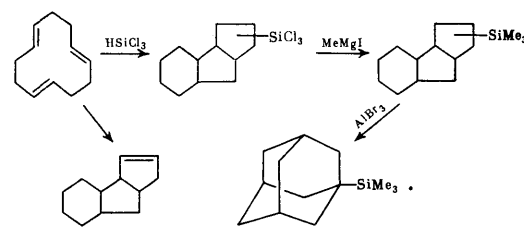
Scheme 1



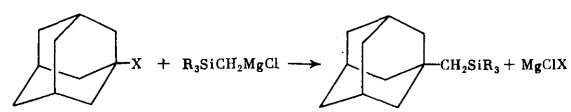
This synthesis has recently been repeated[27], but the trimethylsilyladamantane obtained had a melting point of 236 °C instead of 35 °C.

The isomerisation of a three-membered cyclic compound containing a silyl substituent also yielded trimethylsilyladamantane[28] (Scheme 2):

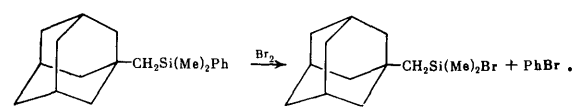
Scheme 2



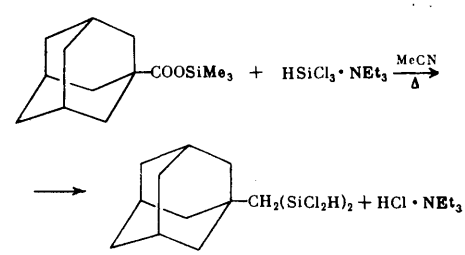
Treatment of chloro- or bromo-adamantane with Grignard reagents obtained from the corresponding α-chloromethylsilanes led to the formation of α-silylmethyladamantanes in good yields (70–80%)[29]:



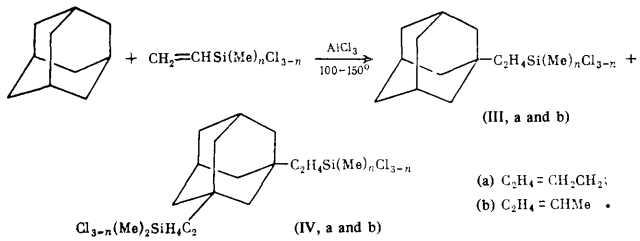
In the presence of the phenyl group at the silicon atom, there is a possibility of obtaining compounds with halogenosilyl substituents:



The Benkeser reaction has also been used to synthesise α-silylmethyladamantanes, but, after treating adamantanecarboxylic acid or its trimethylsilyl ester with the "trichlorosilane–triethylamine" complex in acetonitrile, the product is 1,1-bis(dichlorosilyl)methyladamantane instead of the postulated 1-trichlorosilylmethyladamantane:



The first representatives of α- and β-silylethyladamantanes have been obtained by the Friedel–Crafts reaction[20,30–32]:



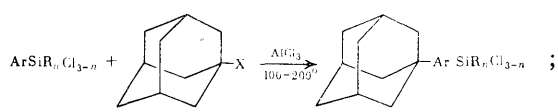
(III, a and b)

(a) $C_2H_4 = CH_2CH_2$;
(b) $C_2H_4 = CHMe$.

(IV, a and b)

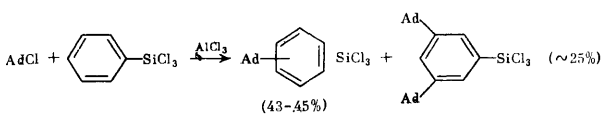
This reaction results in the formation of both 1-monosilyialkylated [compound (III)] and 1,3-bis-silylalkylated [compound (IV)] adamantanes. The ratio of compounds (III) and (IV) is determined by the nature of the unsaturated chlorosilane; for example, 70% of compound (III) and 30% of compound (IV) are obtained from vinyltrichlorosilane, while methylvinyldichlorosilane gives 60% of compound (III) and 40% of compound (IV). After methylation of the mixture of isomers (III, a and b), the isomer having the normal structure (IIIa), which is crystalline, can be readily separated from isomer (IIIb) by freezing out. The silyialkylation of adamantane and 1-chloroadamantane proceeds similarly also under γ-irradiation[13]. In the alkylation of adamantane with trimethylvinyl- and dimethylvinylchlorosilanes this method is also more suitable, because in the presence of aluminium chloride the reaction mixture contains a large amount of tar and it is almost impossible to isolate the adamantane alkylation products.

The Friedel–Craft reaction can also take place between halogenoadamantanes and a number of arylchlorosilanes, despite the fact that the view that phenylchlorosilanes cannot be used in this reaction because of the ready "elimination" of the phenyl group under the influence of Lewis acids has been firmly established in the chemistry of organosilicon compounds for a long time[23,26,33–35]:



X = H or Cl; Ar = phenyl or thienyl; Ar' = phenylene or thienylene.

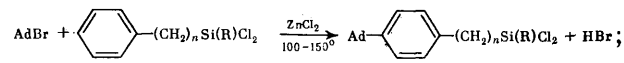
The best alkylation catalyst in the synthesis of adamantylthienylchlorosilanes proved to be tin tetrachloride. The highest yields of adamantyl(phenyl)trichlorosilanes[23,33] have been obtained on heating a mixture of 1-chloroadamantane and phenyltrichlorosilanes in the presence of $AlCl_3$ (in proportions of 4 : 13 : 1) for 3 h at 145–180 °C; under these conditions, up to 25% of *m,m*-diadamantylphenyltrichlorosilane is formed:



(43–45%)

1-Bromoadamantane is more reactive in this reaction than 1-chloroadamantane; in the presence of $AlBr_3$ it interacts with phenyltrichlorosilane even at 30 °C, giving rise to a 60% yield of *p,m*-adamantylphenyltrichlorosilanes[23,35,36]. The use of other catalysts ($ZnCl_2$, $SnCl_4$, and $FeCl_3$) did not lead to the desired results; the starting materials did not react or were converted into a tar.

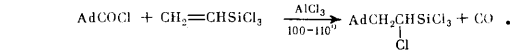
Phenylalkylchlorosilanes of the type $ArR'Si(R)_nCl_{3-n}$ (R' = alkylene) show a greater tendency towards this reaction than phenyltrichlorosilane[36]:



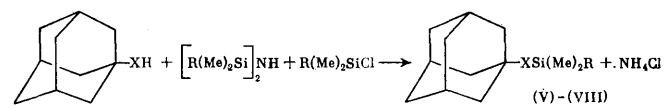
R = Cl or Me; $n = 1, 2$.

The best catalyst for the introduction of the adamantyl group into benzyltrichlorosilane is $ZnCl_2$, while the use of other catalysts ($AlCl_3$ and $FeCl_3$) leads to the formation of products with more than one adamantyl group[37].

No et al.[38] reported an unusual course of the silylalkylation of the chloride of adamantanecarboxylic acid:



Oxygen- and nitrogen-containing silyladamantanes $AdXSiR_3$ (where X = O or N) were obtained for the first time by Mironov and Fedotov[39] by silylating 1-hydroxyadamantane and adamantanecarboxylic acid on heating them with a mixture of hexamethyldisilazane and trimethylchlorosilane:

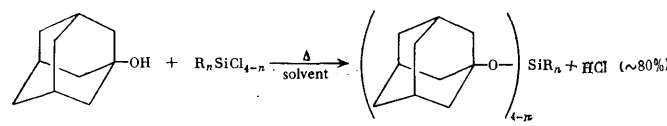


(V)–(VIII)

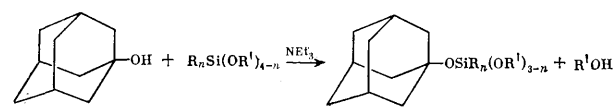
X = O or COO; R = Me[(V), (VI)] or H[(VII), (VIII)].

The authors note that hexamethyldisilazane alone does not silylate 1-hydroxyadamantane even on prolonged heating. It was found later[40–44] that 1-hydroxyadamantane is readily silylated by various chloro- and alkoxy-silanes (Scheme 3):

Scheme 3

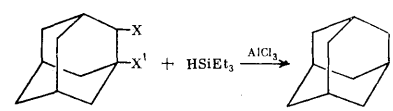


R = CH_2=CH, Ph, or MeO; $n = 0$–3;



R = alkyl, Ph, CH_2 = CH, or $ClCH_2$; R' = alkyl.

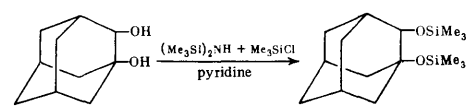
It is of interest that in the presence of Lewis acids triethylsilane reduces 1-bromoadamantane and 2-adamantanol to adamantane[45]:



X^1 = Br, X = H; X = Br, X^1 = H.

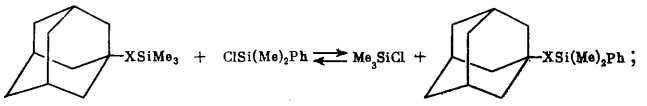
The photoinitiated oxidation of trimethylsilylketen acetal, containing the adamantyl group, to the corresponding peroxyacetate[46] and oxidation of adamantylphenylhydrosilanes with $SnCl_4$ [47] have also been described.

Exhaustive silylation of various dihydroadamantanes proceeds exclusively in pyridine:

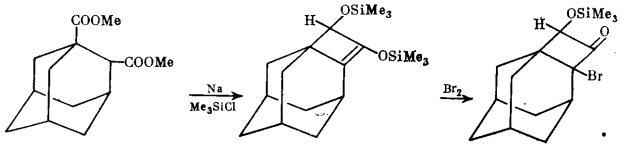


All possible isomers and conformers of bis(trimethylsiloxy)-adamantane were obtained in this way[48] and their NMR spectra were investigated. In addition, it was established that various silyl ethers of 1-hydroxyadamantane and esters of adamantanecarboxylic acid can be readily obtained by the

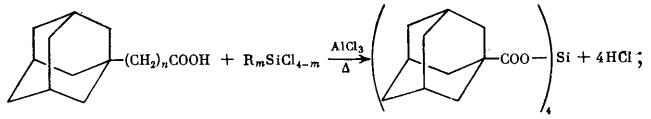
trans-silylation reaction[20,39]:



The silyl ethers of complex alcohols derived from adamantane have been obtained by a modified Ruhlman scheme[49]:

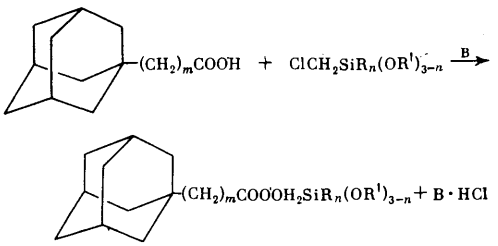


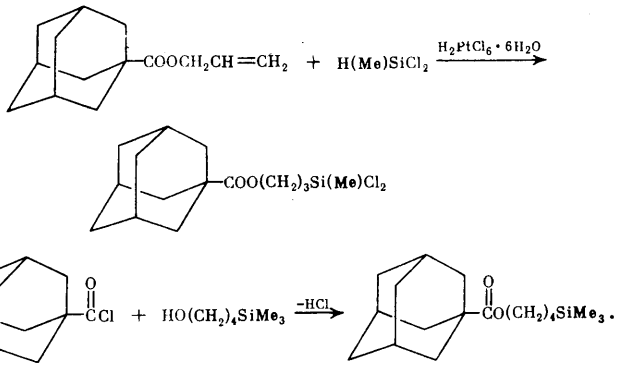
The silyl esters of adamantanecarboxylic acid are readily formed when they interact with chlorosilanes[50,51]:



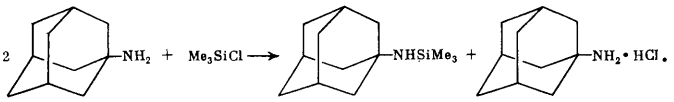
The methods of synthesis of esters of adamantanecarboxylic acids and organosilicon alcohols are illustrated in Scheme 4 below[39,50-53]:

Scheme 4



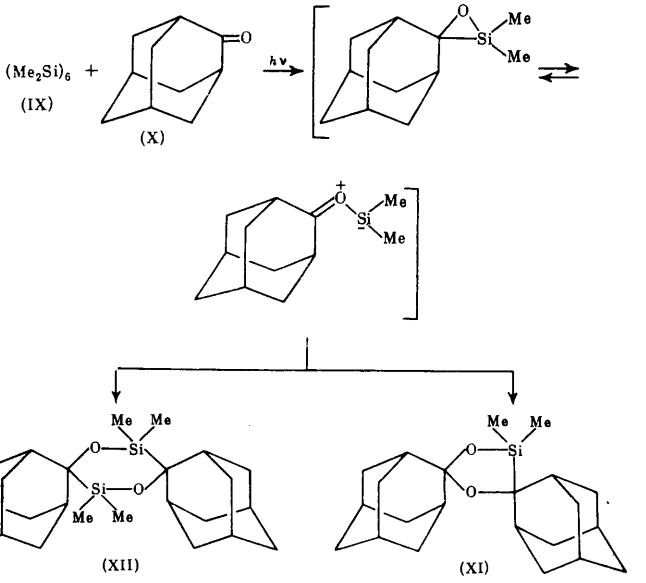


Like the usual primary amines, 1-aminoadamantane is also readily silylated by trimethylchlorosilane[39]:



Japanese investigators[54] obtained dioxasilacyclopentanes with adamantyl groups by the reaction of dodecamethylcyclohexasilane and adamantanone in an ethereal medium under irradiation (Scheme 5).

Scheme 5

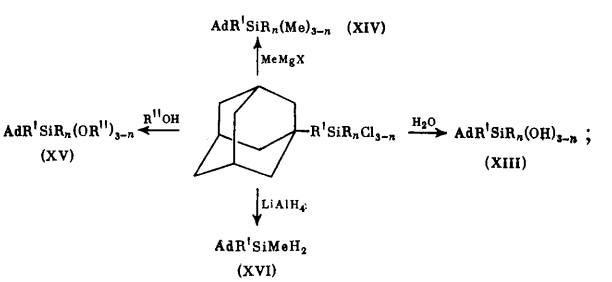


They found[54] that the interaction of compounds (IX) and (X) in the presence of alcohol lead to the formation of $EtOSiMe_2H$ (XI) and 2-ethoxydimethylsilyl-2-adamantanol.

2. Chemical Properties

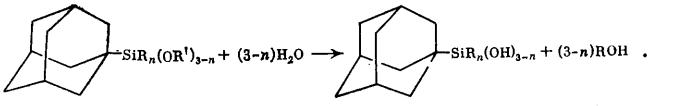
1-Adamantylalkyl(aryl)halogenosilanes are hydrolysed by water and react with alcohols, phenols, and other reagents more slowly than the usual alkyl(aryl)chlorosilanes and form compounds (XIII)[14,15,41,55,56,58], (XIV)[21,23,32,36,58], (XV)[14-16,18,36,37,55-59,61], and (XVI)[29,32,36,58] (Scheme 6).

Scheme 6

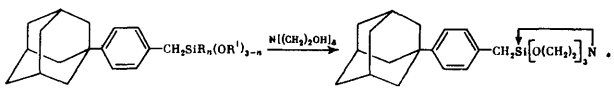


R = alkyl or aryl; R′ = alkylene or arylene; n = 0, 1, 2.

1-Adamantyl(aryl)alkoxysilanes are comparatively resistant to hydrolysis by atmospheric moisture but are readily hydrolysed on heating with dilute alkali in diethyl ether[62]:



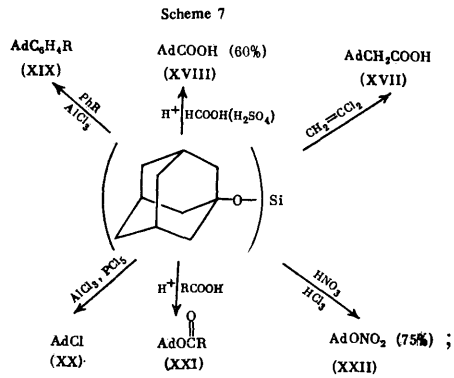
It has been shown[37] that they are readily converted into the corresponding silatranes:



Trimethylsiloxyadamantane is resistant to hydrolysis by cold water but is readily hydrolysed by hot water[39].

The reactions of compounds containing the Ad–O–Si ≡ linkage, particularly tetra-adamantyloxysilane, are illustrated in Scheme 7. A series of adamantane derivatives have been obtained as a result: (XVII)[67], (XVIII)[66–68], (XIX)[40,41,69], (XX)[40,63–65], (XXI)[67], and (XXII)[66]:

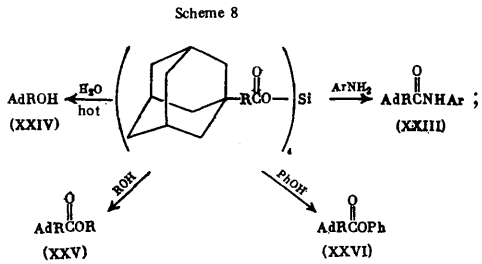
Scheme 7



R = Me, Et, $(Me)_2CH$, or MeO.

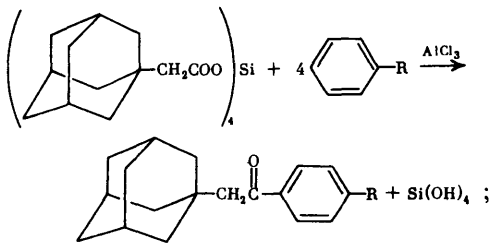
Tetra(1-adamantylcarboxy)silane and tetra(1-adamantylacetoxy)silane have also been investigated in various chemical reactions leading to the corresponding adamantane derivatives: (XXIII)[38,50,51,72], (XXIV)[70,71], (XXV)[70,73], and (XXVI)[73] (Scheme 8):

Scheme 8



Ar = Ph, *o,m*-MeC_6H_4, or $MeOC_6H_4$;
R = Me, Et, n-C_3H_7, n-C_4H_9, iso-C_4H_9, or n-C_5H_{11};
R' = OMe .

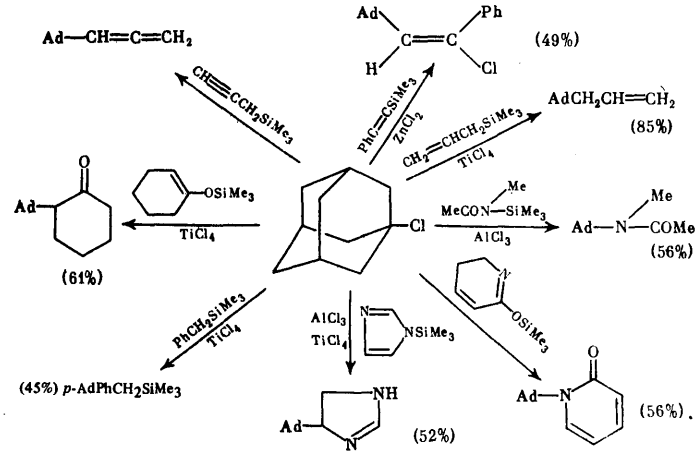
It has been established[42] that tetra(1-adamantylacetoxy)silane is less reactive in reactions with alcohols, 1-adamantanol, and phenol than tetra(1-adamantylcarboxy)silane, but is more reactive in reactions with aromatic amines. Tetra(1-adamantylacetoxy)silane undergoes the Friedel–Crafts reaction with benzene and alkylated aromatic compounds, forming the corresponding 1-adamantyl methyl ketones[42,50]:



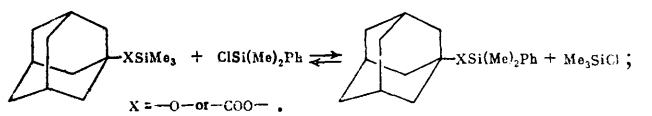
R = Me, Et or $(Me)_2CH$.

Sasaki et al.[74] achieved the interaction of various organic compounds containing trimethylsilyl groups with chloroadamantane in the presence of Lewis acid catalysts. In this way they obtained a number of organic derivatives of adamantane and in only one case a silicon-containing adamantane derivative—*p*-adamantylbenzyltrimethylsilane (Scheme 9):

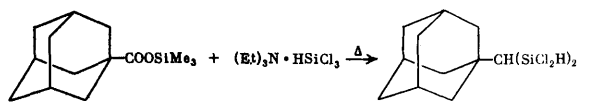
Scheme 9



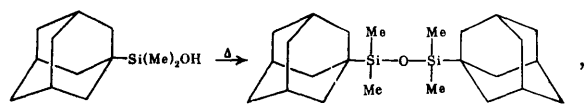
It has been found[39] that, like trimethylsilyl ethers and esters[75], the trimethylsilyl ethers of 1-hydroxyadamantane and the corresponding esters of adamantanecarboxylic acid are capable of undergoing the reversible *trans*-silylation reaction:



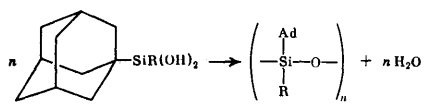
Trimethylsilyl adamantanecarboxylate enters into the Benkeser reaction[24,29]:



The study of the properties of 1-adamantylalkyl(aryl)silanols, obtained by the hydrolysis of the corresponding chloro-, alkoxy-, and acetoxy-derivatives, showed[14] that they are not appreciably dehydrated up to 80–100 °C and are fully dehydrated only at 150–200 °C after 10–15 h. Thus the thermal dehydration of 1-adamantyldimethylsilanol yields the corresponding disiloxane:



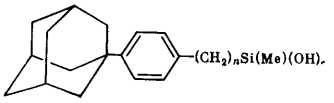
while 1-adamantylalkyl(aryl)silanediols give rise to polymers with the adamantyl group at the silicon atoms, whose molecular weights are in the range 5500–9000:



R = alkyl or aryl.

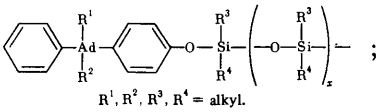
These polysiloxane polymers are resistant to the action of dilute acids and concentrated alkalies at 80–90 °C for 15–20 h.

Novikov et al.[76] obtained monomers of the type



where $n = 1$ or 2, which have been used to synthesise polymers with an increased thermal stability.

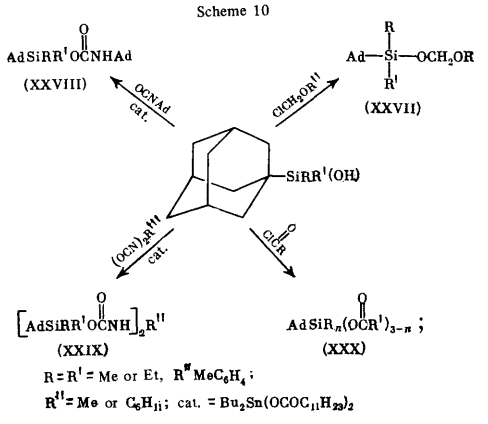
Polysiloxanes containing adamantyl groups of another type have been obtained recently[77]:



R^1, R^2, R^3, R^4 = alkyl.

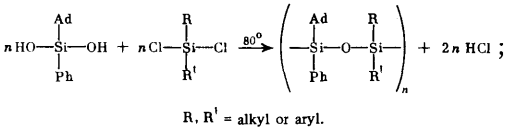
Adamantylsilanols are fairly reactive and react with various reagents, forming the corresponding derivatives: (XXVII)[14,78,79], (XXVIII)[80,81], (XXIX)[82], and (XXX)[83] (Scheme 10):

Scheme 10



R = R' = Me or Et, $R'' = MeC_6H_4$;
R'' = Me or C_6H_{11}; cat. = $Bu_2Sn(OCOC_{11}H_{23})_2$

1-Adamantyl(alkyl)arylsilanols can also undergo the polycondensation reaction with various alkyl(aryl)dichlorosilanes[14,18]:

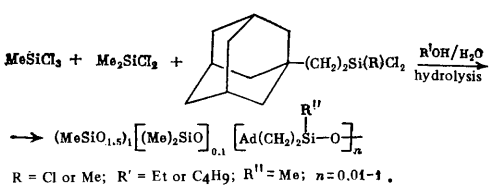


R, R' = alkyl or aryl.

The molecular weights of the polymers thus obtained are 4500–5600, which corresponds to 10–14 elementary units in the chain of the macromolecule.

Cohydrolysis of adamantylalkylhalogenosilanes with the corresponding alkyl(aryl)chlorosilanes made it possible to obtain liquid polysiloxanes—resins with the adamantyl(alkyl)-aryl groups at the silicon atom[84,85] (see, for example, Scheme 11):

Scheme 11



R = Cl or Me; R' = Et or C_4H_9; R'' = Me; $n = 0.01$–1.

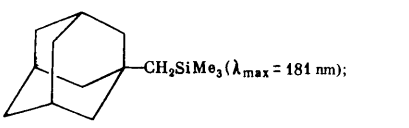
If there are aryl substituents[29] or hydrogen[47,60] in the silyl group of adamantylsilanes, they can be readily substituted by a halogen.

3. Physical Properties

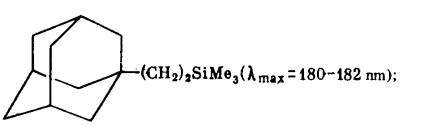
Silyl- and silylalkyl(aryl)adamantanes are as a rule crystalline substances or viscous high-boiling liquids, soluble in the majority of organic solvents. The frequencies of their absorption bands in the infrared spectra are characteristic of both the adamantane structure[86] and of the silyl and siloxane atomic groups linked to it. For example[13], β-(trimethylsilyl)ethyladamantane has a group of bands characteristic of the adamantane structure (970 and 950 cm^{-1}) and also the absorption bands of the Si–H (2120 cm^{-1}) and Si–Me (1800 cm^{-1}) groups.

There are no literature data for the NMR spectra of silyladamantanes, but it is clear that the proton spectra must contain signals due to protons of both the adamantane nucleus and the organosilicon substituents. The ^{13}C NMR spectra, in which it is possible to observe the individual signals of all types of carbon atoms in the molecule, as shown in relation to germyladamantanes[87], contain a particularly large amount of information about the structure. With the aid of ^{13}C NMR, it is possible to determine the position of the silicon-containing substituent in the adamantane skeleton. A satisfactory correlation between the chemical shifts of the ^{13}C NMR signal of the carbon atoms in the adamantane system and the inductive constants of the substituents has been established for substituted adamantanes[88]. The study of ^{29}Si and ^{13}C NMR spectra of mono- and bis-(trimethylsilyl)adamantanols[45] established that the chemical shifts of the ^{29}Si signals of 1- and 2-adamantyl derivatives occur in different regions, the position of the chemical shift being sensitive to steric interactions. This makes it possible to employ the ^{29}Si and ^{13}C NMR methods to establish the structure of any adamantyl derivative after first converting it into the corresponding trimethylsilyl derivative.

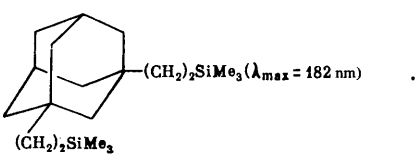
Interesting results have been obtained[89] in the study of the adsorption spectra of both adamantane itself and of silylalkyl(aryl)adamantanes in the far ultraviolet (175–200 nm). It has been established that adamantane has an intense absorption band at 180 nm. Silicon-containing substituents exert a definite influence on the main absorption band: the introduction of trimethylsilylalkylene groups causes a slight shift of the absorption band in the spectra of both mono- and di-substituted adamantanes:



CH_2SiMe_3 (λ_{max} = 181 nm);



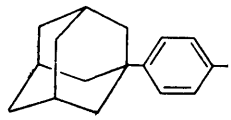
$(CH_2)_2SiMe_3$ (λ_{max} = 180–182 nm);

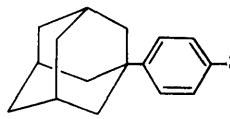


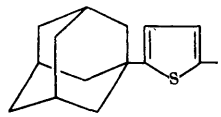
$(CH_2)_2SiMe_3$ (λ_{max} = 182 nm)

$(CH_2)_2SiMe_3$

The introduction of trimethylsilylarylene groups is accompanied by a bathochromic shift.


$SiMe_3(\lambda_{max} = 196$ nm);


$SiCl_3(\lambda_{max} = 197$ nm);


$SiMe_3(\lambda_{max} = 190$ nm)

A mass-spectrometric study[32], carried out in order to determine the isomeric composition of the products of the silylalkylation of adamantane by alkenylchlorosilanes, showed that there is virtually no peak of the $(M-HR)^+$ ion in the mass spectra of all the compounds investigated, while the intensity of the peak of the $(M-R)^+$ ion is high. It is known that 1-substituted adamantanes (Ad–R) typically lose the substituent R in the form of a free radical[90,91], while 2-substituted adamantanes eliminate the MR molecule from the molecular ion[92]. Thus the substituents in all the compounds investigated were either in the 1-position or in the 1- and 3-positions. The spectra of all the mono-substituted adamantanes show the peak of the molecular ion, whose relative intensity increases with increase of the number of methyl groups attached to the silicon atom. The loss of the second substituent from the $(M-R)^+$ ion with migration of the hydrogen atom to the charged fragment, which leads to the formation of the adamantyl cation with *m/e* 135, is characteristic of all substituted adamantanes[32].

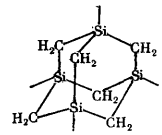
4. The Applications of Silyl- and Silylalkyl(Aryl)-Adamantanes

Silyl- and silylalkyl(aryl)-adamantanes have been synthesised quite recently. The study of their properties as well as the properties of polymers obtained on their bases has been initiated. Nevertheless, in view of the specificity of the properties which polysiloxane polymers acquire after the introduction of adamantyl or adamantylalkyl(aryl)groups, they are already of definite interest as substances with effective stabilities in relation to heat, light, and radiation[84,93].

III. SILA-ADAMANTANES

1. Carborundanes

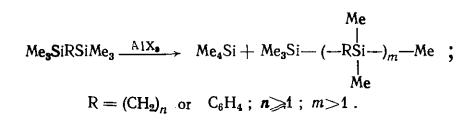
Carborundanes or 1,3,5,7-tetrasila-adamantanes constitute a new class of organosilicon compounds, which have been relatively little investigated and which have extremely unusual physical and chemical properties. The molecular skeleton of tetrasila-adamantane can be regarded as the unit cell of silicon carbide–carborundum (hence the name carborundane), the rigid crystal lattice of which is free from angular and conformational strains, like the diamond lattice:



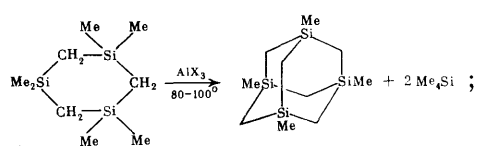
Like diamond, carborundum has exceptional chemical, thermal, and mechanical stabilities. The new class of carborundanes could not therefore fail to interest chemists working in the field of the chemistry of Group IV elements. It might have been expected, in particular, that tetrasila-adamantanes would prove to be extremely promising for the modification of siloxane polymers and for the creation of new thermally and chemically stable materials. At the beginning of 1970 there were only six papers in the literature on the synthesis and properties of carborundanes, while at the beginning of 1980 there were already about 70 original publications and six reviews[11,12,94–97]. However, one should note that the review of Frye and Klosowski[96] is very short and incomplete (the bibliography contains only 11 references), while other reviews are devoted to broader topics—heteroadamantanes[11,12,97] and carbosilanes[94,95], while the information about carborundanes is scanty and non-systematic.

(a) Methods of Synthesis of Carborundanes

There are two methods of synthesising carborundanes. They both consist in a far-reaching degradation of various methylsilanes and silcarbanes (i.e. compounds containing the $\rangle SiCH_2Si\langle$ fragment) under the influence of aluminium halides or on thermolysis. The first method is in fact a development of the reaction of Vdovin[98–100], who discovered the following new reaction in a study of the action of aluminium halides on a wide variety of bridged compounds†:


$Me_3SiRSiMe_3 \xrightarrow{AlX_3} Me_4Si + Me_3Si-(-RSi(Me)-)_m-Me$;
$R = (CH_2)_n$ or C_6H_4 ; $n \geqslant 1$; $m > 1$.

However, the amounts of aluminium halides used in the reaction was so small that it stopped at the stage involving the formation of the silmethylene oligomer[100]. Later Frye and Weyenberg[103] achieved a more far-reaching transformation of various silmethylene compounds into sila-adamantanes under the influence of increased amounts to aluminium halides (20–200% of the weight of the initial compound), for example:


X = Cl or Br.

† This reaction was found subsequently to be fairly general and to occur even when R is oxygen or nitrogen[101]. Furthermore, the reaction is fully characteristic also of the series of analogous organogermanium compounds[102].

Under the reaction conditions, some of the methyl groups at the silicon atom are substituted by the halogen X under the influence of AlX_3, so that Me_3CbX and Me_2CbX_2 are formed together with Me_4Cb. The overall yield of sila-adamantanes for X = Br was 27%.[103] Apart from the six-membered ring, $(Me_2SiCH_2)_n$, where n varies from 2 to 50, $(Me_2XSi)_2CH_2$ (X = Cl or Br), and $Me_3SiCH_2SiMe_3$ have been proposed for the synthesis of carborundanes[104]. The syntheses of sila-adamantanes from $(Me_2SiCH_2)_3$ and $AlBr_3$ (yield 27%), $(Me_2SiCH_2)_2$ and $AlCl_3$, $Me_3SiCH_2SiMe_3$ and $AlCl_3$, and $(Me_2SiCH_2)_n$ and $AlBr_3$ ($n = 4-50$) have been described as specific examples[104]. Furthermore, a mixture of $CbCl_4$ and $MeCbCl_3$ has been obtained from $(Me_2ClSi)_2CH_2$ and $AlCl_3$. The above communications[103,104] contain no data on the properties of the individual sila-adamantanes obtained (yields, melting points, etc.). Frye and Weyenberg apparently did not isolate and purify the substances synthesised. They merely state that the mixtures of sila-adamantanes can be separated by fractional sublimation or adsorption chromatography[104].

Frye's method was developed by other investigators. Thus Fritz and Kreilein[105] showed that, when the heterocycle $(Me_2SiCH_2)_3$ is heated with $AlBr_3$ at 80 °C for 24 h, 18% of Me_4Cb and 1.5% of Me_3CbBr is formed, but, on increasing the reaction time to 72 h and the temperature to 100 °C, the overall yield of desired products falls to 9.5%. Vdovin and coworkers[106] studied the rearrangement of tetramethyldisilacyclobutane under the influence of aluminium halides in greater detail than in Frye's study. They note that Me_4Cb is not formed on treatment with an equimolar amount of $AlCl_3$ at 20 °C; this requires more severe conditions ($AlBr_3$, 70 °C):

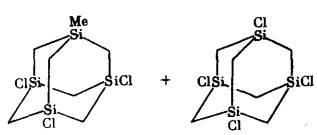
$$(Me_2SiCH_2)_2 \xrightarrow{AlBr_3} Me_4Cb + Me_3SiCH_2SiMe_3 + Me_4Si + \text{oligomers}$$

The yield of Me_4Cb is ~5% on the basis of data quoted by Vdovin and coworkers[106].

The catalytic rearrangements of disilylmethylene compounds $(Me_2SiCH_2)_n$ ($n = 2-11$) have also been studied by Mironov et al.[107]. They established that tetrasila-adamantanes can be obtained from a mixture of oligomers ($n \cong 11$) in a yield not exceeding 4%. The mixture of oligomers is readily formed when $ClCH_2SiMe_2Cl$ is treated with sodium[108] or magnesium[109].

If silmethylene compounds with Si–Cl bonds are used for the synthesis, the reaction with aluminium chloride must be carried out under more severe conditions. For example, the interaction of $(ClMe_2SiCH_2)_2SiCl_2$ with aluminium chloride begins only at 200 °C. The low-boiling products of the rearrangement consist of trimethylchlorosilane and dimethyldichlorosilane (1:2), but the yield of the tetrasila-adamantanes isolated after the reaction is only ~0.3%:

$$(ClMe_2SiCH_2)_2SiCl_2 \xrightarrow[200-215^\circ]{AlCl_3}$$



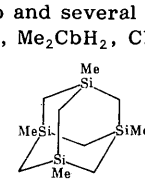
Analogous results are obtained also when the above reaction is carried out in a flow system in the gas phase. The initial chloride together with hydrogen chloride was passed over aluminium filings at 500–600 °C. The yield of sila-adamantanes was ~1% relative to the chloromethylsilane consumed[107]. It was shown experimentally that one of the causes of the low yield of products is the decomposition of the molecular skeleton of methylchlorosila-adamantanes under the influence of aluminium chloride under severe conditions.

Lower methylchlorosilanes can also be used as starting materials for the synthesis of chlorocarborundanes. It is known, for example, that the first representative of the class of 1,3,5,7-tetrasila-adamantanes was obtained by Smith and Clark in 1961[110] as a result of an accidental overheating to 500 °C of an autoclave containing a mixture of trimethylchlorosilane, silicon tetrachloride, and aluminium chloride. Together with six- and eight-membered silmethylene rings, tetrachlorocarborundane ($CbCl_4$) was isolated in 0.1% yield. The substance was not obtained in an analytically pure form, but it was readily characterised with the aid of infrared and ^1H NMR spectra and by determining the molecular weight.

Much later Klosowski and Barry[111] took out a patent for a method of synthesis of sila-adamantanes which is extremely similar to that of Smith and Clark. These compounds are obtained from methylhalogenosilanes Me_nSiX_{4-n} (X = Cl or Br; $n = 1-4$) at 350–450 °C and a pressure of 70–176 atm. The catalyst consists of a mixture of aluminium halide (2.5–15%), silicon, and (or) aluminium (2.5–50% of the weight of the reagents) in order to bind the acid (probably HCl). In the examples described a mixture of Me_2CbCl_2 and $MeCbCl_3$ was obtained from Me_3SiCl, while Me_2SiCl_2 gave mainly $CbCl_4$. The overall yields (according to our calculations based on the data in the patent) are ~13–18%.

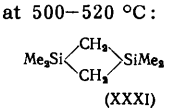
Thus Frye's method gives the best results for low-molecular-weight fully methylated silmethylene compounds, which happen to be the least available silcarbanes. Silmethylene compounds with $SiCl_2$ or $SiCl_3$ groups, which are readily obtained by direct synthesis from chloromethylsilanes $ClCH_2SiRR'R''$, are apparently relatively unsuitable for the synthesis of sila-adamantanes. On the other hand, the lowest methylchlorosilanes are converted into carborundanes only under very severe conditions and with low yields.

There is also another method of synthesis of tetrasila-adamantanes—the pyrolytic method. Thus the tetramethyl derivative Me_4Cb was first detected[112] in the products of the pyrolysis of tetramethylsilane at 700 °C. In subsequent years Fritz and coworkers carried out a laborious and troublesome separation of the very complex mixtures formed in the pyrolysis of Me_4Si,[113-115] $MeSiCl_3$,[116] and Me_3SiCl.[117] The authors published several large monographs and three reviews which describe in detail the methods used to separate and identify the pyrolysis products[94,95,118-121]. It is stated that the most suitable method of fractionating sila-adamantane mixtures is adsorption chromatography[104,113]. The study of the pyrolysis of tetramethylsilane led to the following results: the low-molecular-weight fraction of the reaction mixture consisted of 39 substances containing from one to three silicon atoms in the molecule and also of 12% of Me_4Cb relative to the pyrolysis reaction mixture, which corresponds to a yield of 3%.[115] In the high-molecular-weight fraction (Si_4-Si_8) it was possible to identify[118] ~60% of the compounds, among which Me_4Cb and several of its analogues are again present, i.e. Me_3CbH, Me_2CbH_2, $CbCH_2SiMe_2H$, $CbCH_2SiMe_3$, $CbCH=CH_2$, and

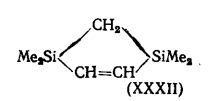


The remaining compounds are complex polycyclic systems of the sila-adamantane types which are described below.

Fritz and Götz[115] established that Me_4Cb is formed in the pyrolysis not only of tetramethylsilane but also of other compounds, for example the heterocycles (XXXI) at 480 °C and (XXXII) at 500–520 °C:



(XXXI)

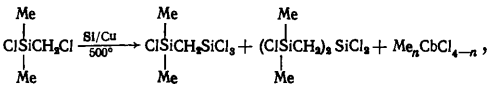


(XXXII)

According to the authors, Me_4Cb is formed via a multistage radical mechanism[115].

The pyrolysis of trimethylchlorosilane leads to a mixture of all four possible chlorosila-adamantanes: $CbCl_4$, $MeCbCl_3$, Me_2CbCl_2, and Me_3CbCl in the proportions 170 : 16 : 3 : 1.[117] The substances were characterised with the aid of ^1H NMR and mass spectrometry.

Finally yet another method of synthesising sila-adamantanes has been discovered recently. In the course of direct syntheses of silcarbanes from α-chloromethylsilanes, for example (chloromethyl)dimethylchlorosilane[122]



it was established that higher-boiling compounds as well as a non-distillable polymeric residue are always formed together with the products indicated. If the initial silane is passed over a mixture of silicon and copper powders at 500 °C, a crystalline deposit, consisting of Me_3CbCl, Me_2CbCl_2, and $MeCbCl_3$, with the dichloride predominating, is precipitated from the still residues. The overall yield of sila-adamantane is ~0.3% relative to the chloromethylsilane passed over the catalyst[107].

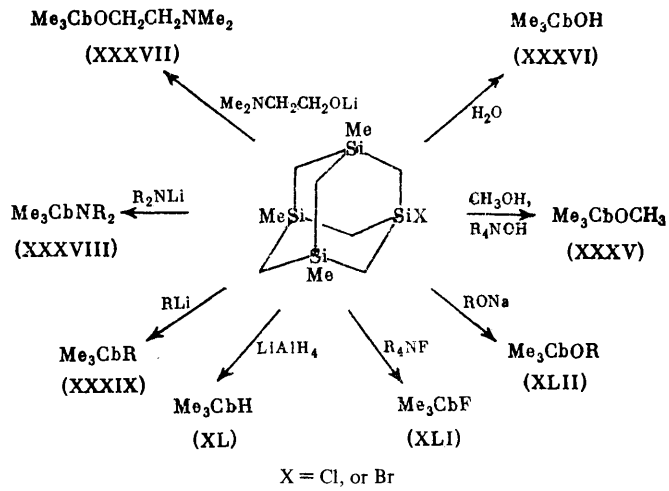
(b) Chemical Properties of Carborundanes

1,3,5,7-Tetrasila-adamantanes have continuously attracted the attention of investigators concerned with problems of the stereochemistry and mechanisms of the reactions involving the silicon atom as the reaction centre. The carborundane molecules incorporate four silicon atoms located in bridgehead positions. The system is rigid and free from angular and conformational strains. According to Sommer[123], such structures should be extremely inert in nucleophilic substitution reactions, because the mechanism involving an inversion of configuration cannot occur and that with retention of configuration is hindered by the rigidity of the cyclic system.

The first results of the study of the reactivity of carborundanes seemingly confirmed this hypothesis. Smith and Clark[110] noted the unusual resistance of $CbCl_4$ to the action of water and methylmagnesium chloride. The monohalides Me_3CbX also proved to be resistant to hydrolysis[124]. The reaction of Me_3CbBr with aqueous acetone takes place over a period of 9 days and the monochloride Me_3CbCl is hydrolysed only by alkali. The bromide is reduced with difficulty by lithium tetrahydroaluminate and the analogous reaction with the chloride takes place to an extent of only 10%.[124] It was found that $MeCbCl_3$ and $CbCl_4$ are only partially reduced by the $LiH–LiAlH_4$ mixture[117], while the mono-and di-chlorides do not react at all. However, it has been established that Me_3CbCl reacts with lithium derivatives of dialkylamines and dimethylaminoethanol. One should note particularly the fact that the derivatives obtained, containing the Si–N or Si–O bond in their molecule, which are usually hydrolytically unstable, in the present case were not hydrolysed even with hydrochloric acid[124].

The publication of the above studies was soon followed by the appearance of the paper of Homer and Sommer[125], who claimed that their results are in sharp conflict with the established view that the reactivity of the sila-adamantane system in relation to nucleophiles is reduced. Indeed, they obtained Me_3CbOMe and Me_3CbF in high yields (86–90%) (see Scheme 12).

Scheme 12



$Me_3CbCl \xrightarrow{LiH/LiAlH_4}$ does not react (Ref.117),

$Me_2CbCl_2 \xrightarrow{LiH/LiAlH_4}$ does not react (Ref.117),

$MeCbCl_3 \xrightarrow{LiH/LiAlH_4} MeCbCl_2H + MeCbH_3$[117],

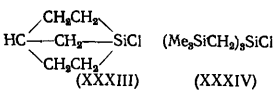
$CbCl_4 \xrightarrow{LiH/LiAlH_4} CbCl_3H + CbH_4$[117],

$Me_3CbOCH_3 + (iso\text{-}C_4H_9)_2AlH \longrightarrow Me_3CbH$[125, 127],

$Me_2CbCl_2 + CH_3ONa \longrightarrow Me_2Cb(OCH_3)_2$[127],

$CbBr_4 + Me_3SiCH_2Li \longrightarrow (Me_3SiCH_2)_4Cb$[105].

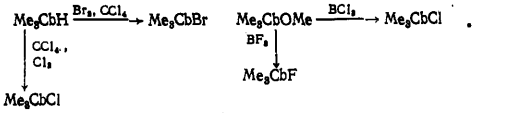
The alkylation of Me_3CbX with phenyl- and methyl-lithium was also found to be possible, although in the latter case the presence of tetramethylethylenediamine, which activates methyl-lithium, was necessary. Furthermore, Me_3CbOMe is readily reduced by di-isobutylaluminium hydride in ether, while its acyclic analogue $(Me_3SiCH_2)_3$–SiOMe reacted 100 times more slowly[125]. It is noteworthy that all these reactions with nucleophiles has been studied earlier by Sommer and coworkers in relation to acyclic optically active silicon compounds. The results of the study of the stereochemistry and mechanisms of these reactions are surveyed in a book[123] and in a review[126]. The use of data accumulated in this field enabled Homer and Sommer[125] to put forward certain hypotheses concerning the mechanism of the interaction of sila-adamantanes with nucleophiles. Subsequently these reactions were studied more thoroughly by the authors; the reactivity of the sila-adamantane system was compared with those of two model compounds (XXXIII) and (XXXIV)[127]:



The authors concluded that their results are best explained by the interaction of Me_3CbX with the nucleophiles investigated in terms of the S_N2–Si mechanism, which postulates a considerable involvement of the *d* orbitals of silicon and operates with retention of configuration. On the other hand, the reduction of Me_3CbOCH_3 by di-isobutylaluminium hydride probably proceeds via the S_Ni–Si mechanism involving a four-centre transition state[127]. All the reactions involving the nucleophilic substitution of tetrasila-adamantanes known

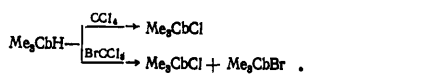
at present are surveyed in Scheme 12: (XXXVI), (XXXVII),[124] (XXXVIII),[124,128] (XXXV),[125,127] (XXXIX),[105,125,127] (XL),[124,127] and (XLI)–(XLII).[125,127]

Homer and Sommer established[129] that tetrasila-adamantanes react fairly vigorously also with certain electrophiles. For example, the halogenation of Me_3CbH takes place rapidly in the cold in scattered light, while the interaction of the methoxy-derivative with BCl_3 takes place instantaneously:

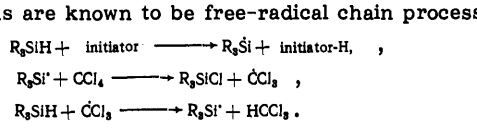


It had been shown earlier[123] that the analogous reactions with acyclic organosilicon compounds take place with retention of configuration. Evidently this type of process is not interfered with by the specific geometry of the sila-adamantane system. The interaction of Me_3CbOMe with BF_3, which goes to completion in six days, contrasts sharply with the halogenation of this sila-adamantane by boron trichloride[129]. According to Sommer's data[123], the analogous reaction of acyclic alkoxysilanes is accompanied by the inversion of configuration. This mechanism is impossible for the sila-adamantane system, so that the reaction with BF_3 proceeds, according to the hypothesis of Homer and Sommer[129], via some other pathway, least favourable as regards the nature of the reagent.

Homer and Sommer established[130] that the rigid geometry of sila-adamantanes does not hinder the formation and reactions of radicals produced from Me_3CbH under the influence of benzoyl peroxide:

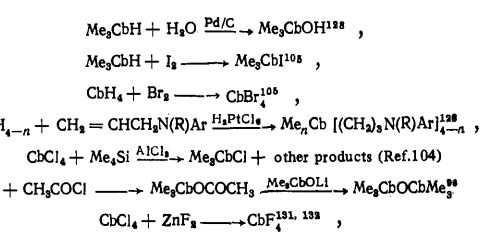


Such reactions are known to be free-radical chain processes:



It has been found[130] that the compound $(Me_3SiCH_2)_3SiH$, which is an acyclic analogue of Me_3CbH, reacts much more slowly with CCl_4; consequently the radical $Me_3Cb^{\cdot}$ is formed faster than $(Me_3SiCH_2)_3Si^{\cdot}$. The selectivity of the radical $Me_3Cb^{\cdot}$ in the elimination of a halogen atom from $BrCCl_3$ proved to be approximately the same as that of other silyl radicals (this has been inferred in relation to the Me_3CbCl and Me_3CbBr formed)[130].

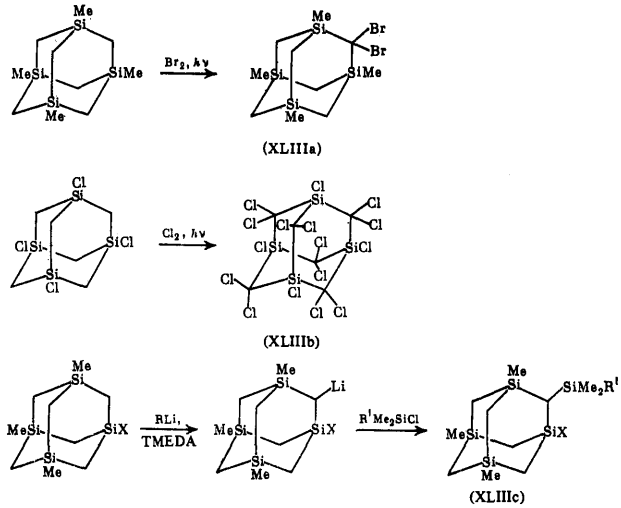
In conclusion certain other reactions of carborundanes may be mentioned:



In contrast to the fluorination of Me_3CbX by quaternary ammonium salts (Scheme 12), the reactions with ZnF_2 have been carried out under more severe conditions (in the absence of solvents at 100–160 °C).

Recently Fritz and coworkers[105,131] discovered a new property of carborundanes—the ability to be halogenated and metallated at the ring carbon atom [Scheme 13; (XLIIIa),[105] (XLIIIb),[131] (XLIIIc)[105]].

Scheme 13



X = Me or halogen; R = n-C_4H_9 or CH_2SiMe_3; R′ = Me or Ph; TMEDA = $Me_2NCH_2CH_2NMe_2$.

A further two trimethylsilyl groups were introduced in succession into the last compound (XLIIIb, R′ = Me) with the aid of butyl-lithium[105].

Thus the geometry of the relatively rigid ground state of the tetrasila-adamantane system does not prevent the reactions with radical reagents and the majority of nucleophiles and electrophiles and permits the synthesis of various derivatives of tetrasila-adamantanes. The chemical properties of sila-adamantanes are discussed by Frye's review[96], which summarises mainly the results of his own studies and those of his coworkers. However, attention is concentrated[96] on the mechanism of the rearrangement of silmethylene compounds to tetrasila-adamantanes under the influence of AlX_3 and also on the problem of "oxasila-adamantane" (see below).

(c) Physical Properties of Carborundanes

1,3,5,7-Tetramethyl-1,3,5,7-tetrasila-adamantane and its halogeno-derivatives Me_nCbX_{4-n} are colourless crystalline readily sublimed compounds with a sharp smell. Despite their high molecular weights and frequently very high melting points, the majority of sila-adamantanes can be analysed by gas–liquid chromatography. Fritz[121] also notes the high thermal stability of Me_4Cb: at 520–540 °C this substance remains unaltered for 37 h.

Various physicochemical methods have been used to investigate the catalytic characteristics of the structure of sila-adamantanes. It has been shown by X-ray diffraction of Me_4Cb [133] that the average length of the Si–C bond in the $Si-CH_3$ and $Si-CH_2$ groups is respectively 1.889 and 1.866 Å, which is within the usual limits for the silicon–carbon bond in organic compounds of silicon. An analogous study of Me_3CbBr [134,135] led to the following results: the Si–C bond lengths are 1.84–1.90 ± 0.02 Å and the Si–Br bond length is 2.15 ± 0.01 Å. A quantum-chemical calculation of the geometrical parameters of the Me_4Cb molecule has been carried out[136].

The photoelectron spectra of the compounds CbX_4 (X = Me, H, F, or Cl) have been investigated[137,138] and it was found that the sila-adamantane molecules, like those of adamantane and urotropine, are not entirely free from strain, which is

due to the transannular SiC–SiC– and CH_2–CH_2-interactions. However, such interactions are 2–3 times weaker than in adamantane owing to the greater length of the Si–C bond compared with C–C. The changes in the spectra of the series of organosilicon compounds are induced by the inductive effect of the substituent. No influence of the $p\pi - d\pi$ interaction on the photoelectron spectra of sila-adamantanes has been observed.

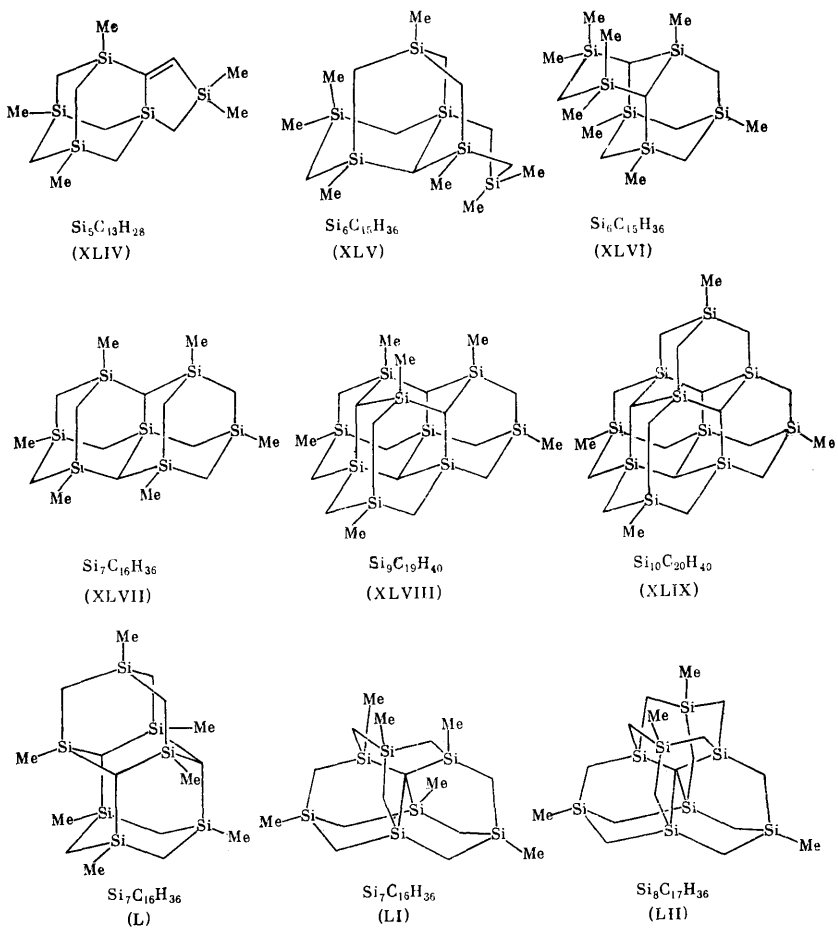
The infrared[110,124,127], ^{1}H NMR [103,105,110,115,118,124,127,131,132,139], and mass spectra[103,105,117,124,127,131] have been studied mainly in order to identify the compounds obtained. However, there has been one investigation specially devoted to the vibrational spectra of 1,3,5,7-tetramethyl-1,3,5,7-tetrasila-adamantane[140], whose author assigned the observed bands to the types of vibrations and carried out a number of calculations. The force constants obtained were compared with data for other organosilicon compounds.

The mass spectrum of $CbCl_4$, showing the presence of an intense $(M-15)^+$ peak, has been studied in greatest detail[141]. The authors noted that the appearance of this ion is probably associated with complex rearrangements of the skeleton requiring the dissociation of not less than three bonds.

Interesting results have been obtained in the determination of the basicity of Me_3CbNEt_2 in an aqueous medium and on comparing it with the basicities of other organic amines[142]. In view of the hydrolytic stability of the Si–N bond in the silylamine investigated, it was possible to achieve this for the first time. It was found that the basicity of the silylamine Me_3CbNEt_2 is much lower than those of triethyleneamine and 1-aminoadamantane. The authors[142] note that such decrease of the basicity of silylamines compared with their organic analogues is usually accounted for by the $d\pi - p\pi$ bonding in the ground state of the former, although one cannot rule out the possibility of the phenomenon, formulated by Pauling, as the neighbouring charge rule. It was shown in the above study that there is no appreciable 1,3-$(d-d)$ interaction in the molecules of sila-adamantanes in the excited state, the possibility of which for compounds with the Si–CH_2–Si group had been postulated earlier. This is confirmed by the results of a study of the ultraviolet spectra of $PhCbMe_3$ and Ph_2.$CbMe_2$; both phenyl groups in the latter compound proved to be electronically isolated, which indicates the absence of 1,3-$(d-d)$ interaction in this sila-adamantane nucleus[142].

(d) Applications of Carborundanes

Patents[104,111] recommend that Me_nCbX_{4-n} mixtures be used as mosquito repellents. It has been suggested that nitrogen-containing tetrasila-adamantanes be employed as emulsifying additives[128].



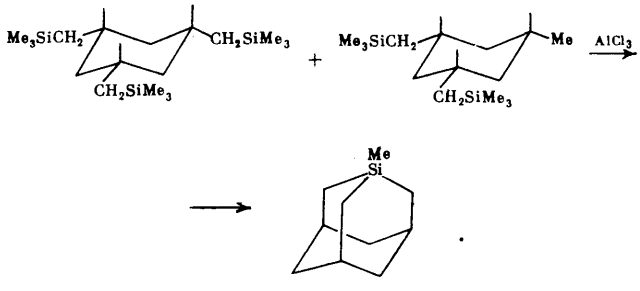
Compounds (XLIV)–(XLVII) and **(L)–(LII) according to the** data of Fritz and Marquardt[118] and compounds (XLVIII) and (XLIX) **according to the data of Fritz et al.**[113].

2. Higher Homologues of Carborundane

A number of higher homologues of Me_4Cb were obtained for the first time by Fritz from the pyrolysis products of tetramethylsilane[113,114,118]. Depending on the details of the steric structure, the authors separated these substances into two classes—"carborundanes" and "silascaphanes". Fritz used the latter name to designate polycyclic compounds belonging to a previously unknown class containing, together with the six-membered rings in the "chair" form, one or more rings in the "boat" form#[143]. Among the group of compounds (XLIV)–(XLIX) of the first type (see Figure), compound (XLVII), whose melting point and the relevant mass-spectrometric data[113,114] have been published and whose ^1H NMR [114] and photoelectron[138] spectra have been studied in detail, has been characterised most fully. The silascaphanes (L)–(LII) have been characterised in terms of the melting points, ^1H NMR data, and mass spectra[143]. Compound (LII) has been studied by X-ray diffraction[144].

3. Other Classes of Sila-Adamantanes

A compound with a single silicon atom in the adamantane nucleus has been synthesised recently[145]:

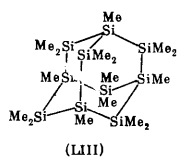


The structure of 1-methyl-1-sila-adamantane has been established by electron diffraction in the gas phase[146].

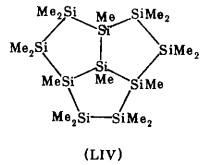
The class of sila-adamantanes includes also a group of adamantane-like compounds whose skeleton consists either of silicon atoms or of silicon and other atoms (for example, oxygen, sulphur, selenium, or phosphorus atoms). The compound $Si_{10}Me_{16}$ is of interest as a possible structural analogue of the adamantane whose skeleton consists of silicon atoms. It has been synthesised[147,148], together with other bicyclic and cellular compounds, by the reaction

$$Me_2SiCl_2 + MeSiCl_3 + Na/K \xrightarrow[C_{16}H_{34}]{THF} (MeSi)_n(Me_2Si)_m + Na(K)Cl$$

Mass-spectrometric, NMR, and infrared spectroscopic data established that the compound consists of a mixture of two postulated structural forms (LIII) and (LIV) in proportions of 3:1; the melting point of the mixture is above 360 °C.



(LIII)

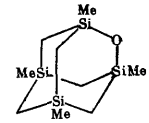


(LIV)

According to original papers, all the rings are in the boat form in silascaphanes.

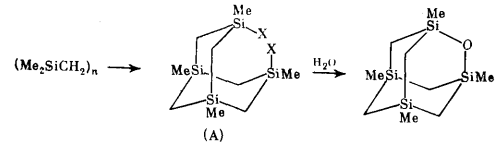
However, a final conclusion concerning the structure of $Si_{10}Me_{16}$ will be possible only after careful studies and X-ray diffraction analysis.

Sila-adamantanes in which one or several carbon atoms have been substituted by oxygen, sulphur, selenium, and phosphorus atoms have now been obtained. One such compound, 1,3,5,7-tetrasila-8-oxa-adamantane (LV), has been isolated by Fritz and coworkers[112,118] from the pyrolysis products of tetramethylsilane and characterised in terms of its mass and ^1H NMR spectra.



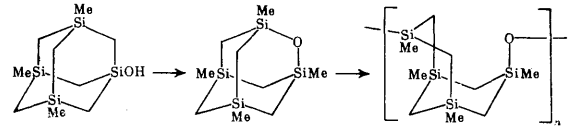
(LV)

The same compound as well as its chloro- and bromo-derivatives have been synthesised by Klosowski[149], who used Frye's method for this purpose[104]—the catalytic rearrangement of silmethylene derivatives of the type $(Me_2SiCH_2)_n (n \geq 2)$ and $(Me_2XSi)_2CH_2$ (X = Cl, Br, or Me) in the presence of aluminium halides. In his paper[149] and also in Frye's review[96] it is stated that in certain cases (these are not specified) the reaction mixture contains after rearrangement a side product having a postulated structure A, which leads to oxasila-adamantanes after hydrolysis:



(A)

According to Frye and Klosowski[96], oxasila-adamantanes can be formed in certain cases also as a result of the rearrangement of Me_3CbOH:

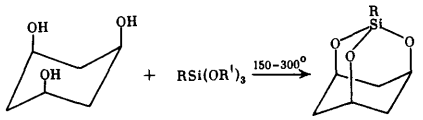


Their attempts[96] to obtain the silanol Me_3CbOH by heating $Me_3CbOCH_2CH_2NEt_2HCl$ in a highly acid medium led to a polymeric product, which may be formed as a result of the above reactions[96].

Klosowski[149] claims that the content of oxatetrasila-adamantanes in the mixture can be increased by carrying out the reaction in the presence of halogenating agents of the type of MeCOX (X = Cl, or Br) and Me_nSiX_{4-n} (X = Cl or Br, n = 1–3). It is suggested that these additives increase the yield of the products (A) and lead to oxasila-adamantanes in which one of the substituents at the silicon atom is chlorine or bromine. The authors note that, in contrast to the structure of the usual tetrasila-adamantanes, the structure of oxasila-adamantanes is apparently not free from strain, since the vibrational frequency of the Si–O–Si linkage is appreciably reduced. It is extremely likely that this structure will be readily polymerised with ring opening[96,149].

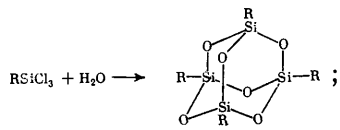
A method of synthesis of 3-substituted 2,4,10-trioxa-3-sila-adamantanes, consisting in the interaction of *cis*-phloroglucitol with trialkoxysilanes in the presence of triethylamine

on heating has been described[150,151]:



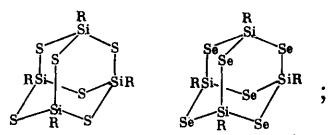
R = Me, Ph, or CH_2=CH; R' = Me or Bu.

Adamantanes of the purely siloxane type have been obtained by the hydrolysis of t-butyl and isopropyl-trichlorosilanes[152]; as a result of their high volatility, these compounds were isolated by sublimation from solid polymeric hydrolysis products. Their compositions and structures were established by elemental analysis and by molecular weight determinations (cryoscopically):



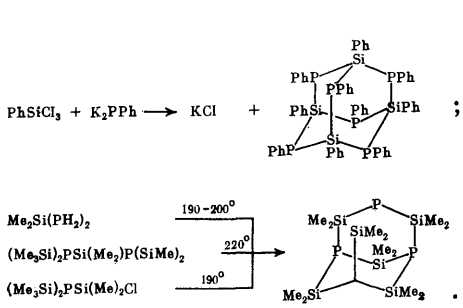
R = iso-Pr or t-Bu .

Analogous thiatetrasila- and selenatetrasila-adamantanes have been obtained under severe conditions from alkylsilanes or alkyltrichlorosilanes and hydrogen sulphide and hydrogen selenide respectively[153] and also from phenylsilane and sulphur[154].



R = Me or Et.

The crystal and molecular structures of the methyl derivative $(MeSi)_4S_6$ have been studied[155,156]. Compounds with a silicon–phosphorus adamantane nucleus have been obtained[157,158] by the reactions



IV. GERMYL- AND GERMA-ADAMANTANES

The first representative of germyladamantanes was obtained in 1973 [19]:

$$AdX + GeX_4 \xrightarrow{Na} AdGe\ (26\%)\ .$$

However, the Wurtz reaction, used successfully in this instance, proved to be relatively unsuitable for the synthesis of other germyladamantanes.

The unexpectedly easy condensation of 1-halogenoadamantanes with trihalogenogermane etherates was discovered in 1974 [87,159]:

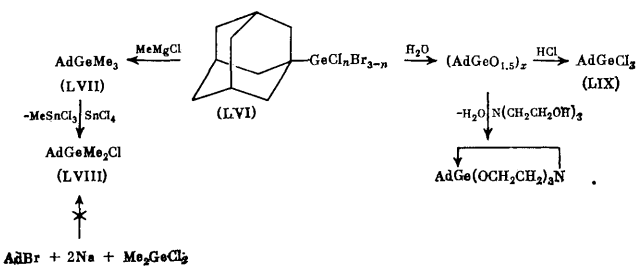
$$AdX + HGeX_3 \cdot 2Et_2O \xrightarrow[-HX]{80^\circ} AdGeX_3 + Et_2O\ ;$$

X = Cl or Br.

In contrast to the condensation reactions with acyclic tertiary halides, the interaction of the etherates with 1-halogenoadamantanes proceeds slowly after prolonged refluxing of the reaction mixture. This factor is the cause of the low yield of 1-tribromogermyladamantane, since the etherate $HGeBr_3$ decomposes to ethanol and $C_2H_5GeBr_3$ after prolonged heating. Use of the more stable etherate $HGeCl_3$ leads to a high yield of the product (75%). When the etherate $HGeCl_3$ reacts with 1-bromoadamantane, a mixture of chloro(bromo)germyladamantanes $AdGeCl_nBr_{3-n}$ ($n = 0-3$) is formed in ~70% yield. When the etherate of trichlorogermane is replaced in this reaction by its aminate $Et_3N.HGeCl_3$, the yield is sharply reduced (to 10%) after the same reaction time and at the same temperature[87,159].

Certain reactions of trihalogenogermyladamantanes have been carried out (Scheme 14).

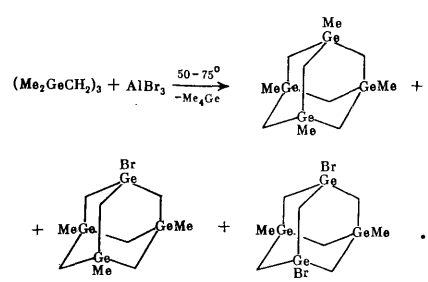
Scheme 14



It was found[87] that the presence of the adamantyl group does not introduce significant changes into the chemical behaviour of the functional groups linked to the germanium atom. The unusually slow and incomplete reaction involving the formation of 1-adamantylgermatrane compared with the synthesis of alkyl- and phenylgermatranes by a similar method is noteworthy[160]. The reaction between compound (LVII) and $SnCl_4$ takes place very selectively, leading to the elimination of the methyl and not the adamantyl group under relatively mild conditions. Thus a compound with the Ad–Sn bond could not be obtained. In the synthesis of compound (LVIII) by an independent method via the Wurtz reaction mainly the reduction of the bromoadamantane to adamantane was observed. Traces of compound (LVIII) were detected only chromatographically.

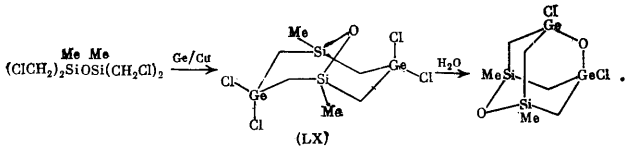
The structure of the germyladamantanes obtained was investigated by NMR[87]. Since the proton spectrum of the adamantane group is extremely complex and cannot be interpreted, ^{13}C NMR was used to investigate compounds (LVI)–(LIX).

The first representatives of 1,3,5,7-tetragerma-adamantanes have been obtained by a method analogous to that for the synthesis of carborundanes[161,162]:



It was established that, with increase of temperature and the reaction time, the monobromo-derivative is formed almost exclusively, with a slight admixture of the dibromo-compound. When bis(trimethylgermyl)methane was used as the starting material, the product proved to be a mixture of all three germa-adamantanes.

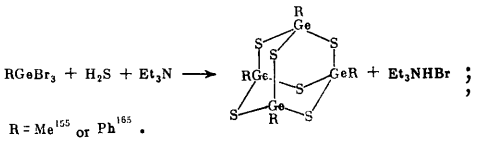
The attempts to synthesise a mixed oxasilagerma-adamantane have been reported[162-164]:



(LX)

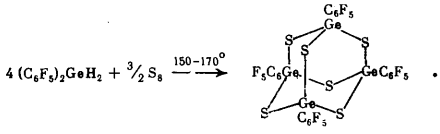
However, the products obtained in the last reaction stage contained only traces of the required compound, which were detected mass-spectrometrically. This is probably due to the steric structure of the intermediate bicyclic compound (LX) which is unfavourable for ring closure; the compound has the "chair–boat" conformation in the crystalline state[164].

Sulphur-containing germa-adamantanes have been obtained by the reaction

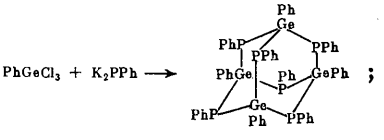


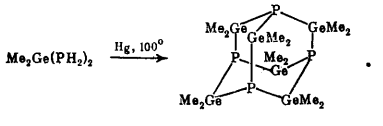
R = Me[155] or Ph[165].

The adamantane-like structure of the high melting crystalline products isolated was demonstrated by mass-spectrometric, infrared spectroscopic, and ^{1}H NMR data as well as X-ray diffraction[155,165]. An analogous derivative has been synthesised by Bochkarev et al.[166]:



Two-different phosphorus-containing germa-adamantanes have been synthesised[157,167]:





V. STANNYL- AND STANNA-ADAMANTANES

An adamantyl derivative of tin was obtained for the first time simultaneously by two groups of investigators[168,169], who studied the stereochemistry of the interaction of Me_3Sn anions with different organic halogeno-derivatives:

$$Me_3SnM + AdBr \longrightarrow Me_3SnAd \ ;$$

Me = Na, K, or Li

In addition, it has been claimed[169] that not only 1-bromoadamantane but also the 2-bromo-derivative forms readily the corresponding adamantyltrimethylstannane under analogous conditions. Evidently in the case of the sterically rigid 1-adamantyl group the reaction proceeds with retention of configuration. To account for this finding, a two-stage reaction mechanism has been proposed[168,169]:

$$Me_3SnM + AdBr \xrightarrow{slow} Me_3SnBr + AdM$$

$$\downarrow \text{fast}$$

$$M = Na \text{ or } K. \qquad Me_3SnAd + MBr$$

According to Koermer et al.[168], nucleophilic S_N2 substitution at the halogen atom takes place in this instance. Later Roberts[19] repeated the synthesis of Me_3SnAd with the aid of an analogous reaction. Other derivatives (Me_2SnAd_2, Ph_2. $SnAd_2$) could not be obtained by this method, but the Wurtz reaction has been used successfully[19]:

$$Ph_3SnCl + Na + AdCl \longrightarrow Ph_3SnAd \ (19\%) \ ;$$

$$SnCl_4 + Na + AdCl \longrightarrow Ad_4Sn \ (20\%) \ .$$

The compounds obtained were characterised in detail by elemental analysis, melting point measurements, infrared spectra, and NMR.

According to Roberts' hypothesis[19], the Wurtz reaction takes place in this instance via a radical mechanism involving electron transfer from sodium to R_3SnX and AdX:

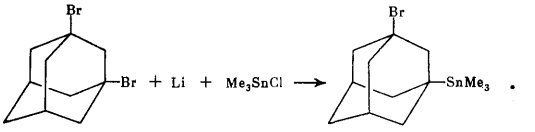
$$R_3SnX + Na^{\cdot} \longrightarrow R_3Sn^{\cdot} + NaX \ ;$$

$$AdX + {}^{\cdot}Na \longrightarrow Ad^{\cdot} + NaX \ ;$$

$$R_3Sn^{\cdot} + Ad^{\cdot} \longrightarrow R_3SnAd \ .$$

It has been stated[19] that the process is accompanied by side reactions involving the dimerisation of the radicals with formation of Ad_2 and R_3SnSnR_3. The attempts to synthesise 1-adamantyltrichlorostannane by refluxing 1-chloroadamantane and $SnCl_2$ in diglyme (with and without the addition of amine salts as catalysts) were unsuccessful: mainly the reduction of chloroadamantane to adamantane was observed[87].

3-Bromo-1-trimethylstannyladamantane has also been synthesised[170]:



Certain chemical properties of adamantyl derivatives of tin have been investigated[19,171], mainly in reactions with electrophiles. The tetra-adamantane compound proved to be extremely inert with respect to bromine and $HgCl_2$. However, the same reagents interact vigorously with monoadamantyl derivatives:

$$Me_3SnAd + X_2 \longrightarrow Me_2XSnAd \ ;$$

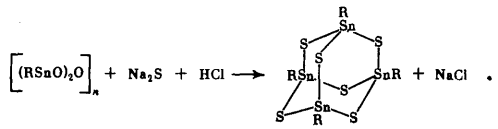
$$Me_3SnAd + HgCl_2 \longrightarrow Me_2ClSnAd \ ;$$

X = Cl or Br.

Triphenyladamantyltin reacts with bromine exclusively with the dissociation of the tin–phenyl bond.

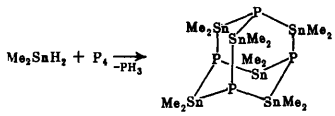
The physical properties of adamantylstannanes have so far been studied inadequately. Roberts[19] quotes the wavelengths of the infrared absorption bands of Me_3SnAd and Ph_3SnAd as well as ^{1}H and ^{13}C NMR data for the compounds synthesised (certain features of the proton spectra are also discussed). Several sulphur-containing adamantane-like compounds of tin have also been obtained. Komura and Okawara[172] investigated the reactions of methyl-, n-propyl-, and n-butyl-tin oxides with sodium sulphides in hydrochloric acids. The reaction of

the n-butyl compound yielded a product soluble in benzene, which made it possible to determine its molecular weight and to study some of its chemical properties:

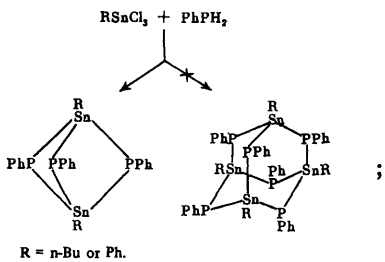


Later this compound was suggested as a stabiliser of PVC.[173] The methyl derivative (R = Me) obtained from $MeSnCl_3$ and Na_2S has an analogous structure[174] However, the adamantane-like structure of the compound obtained was established by X-ray diffraction much later[175].

Selenium- and tellurium-containing stanna-adamantanes $Me_4Sn_4X_6$ (X = Se or Te), whose structure was confirmed by infrared spectroscopic NMR, and X-ray diffraction data, were synthesised from $MeSnBr_2$ and NaHX.[176] A novel hexakis(dimethylstannyl) tetraphosphide has been obtained recently[177]:



It is noteworthy that the attempt to synthesise another phosphorus-containing stanna-adamantane was unsuccessful[155], although the analogous reactions with organosilicon and organogermanium compounds led to products with the adamantane structure:



R = n-Bu or Ph.

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During the preparation of the manuscript for the press, new reports on the chemistry of silicon-containing adamantanes were published. Among the new syntheses of silyladamantanes, the involvement of dihalogenoadamantanes and arylsilanes in the Friedel–Crafts reaction[178,179] as well as the interaction of adamantane with methylchlorosilane under the influence of lithium[180] should be mentioned. Polymers have been obtained from silyladamantanes; they exhibit improved thermal and radiation stabilities[181]. The structure of 1-methyl-1-sila-adamantane has been established by gas electron diffraction[182,183]. Studies on tin-substituted adamantanes are being continued: the methods of synthesis are being improved and the physicochemical properties (^{13}C NMR spectra) and the chemical behaviour of these compounds are being investigated[184].

Reports of the synthesis of a new inorganic high-strength fibre from silicon carbide, suitable for the preparation of a wide variety of compound materials, have recently begun to appear in the literature[185,186]. The technology of the preparation of this fibre consists in the spinning of thread from a polymeric oxygen-free organosilicon product and its subsequent thermal carborundation[187–189].

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Fluorine-containing Halogenomethylenephosphoranes

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The methods of synthesis of fluorine-containing halogenomethylenephosphoranes, their stability, and their applications in the Wittig reaction in order to obtain fluorine-substituted olefins are examined.
The bibliography includes 80 references.

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I. INTRODUCTION

Phosphorus ylids are widely used in organic synthesis[1-7], mainly in order to obtain various unsaturated compounds by the Wittig reaction. In recent years phosphorus ylids containing fluorine or fluorinated residues in the methylene group have been used on an increasing scale. The properties of fluorine-containing phosphorus ylids and the methods of their generation depend on the relative positions of the fluorine atoms and the carbanionic centre of the methylene group.

Fluorine-containing halogenomethylenephosphoranes, which are the subject of the present review†, constitute a special group of such phosphorus ylids.

Fluorine-containing mono- and di-halogenomethylenephosphoranes (I, a–h) are apparently insufficiently stable for their isolation in a pure form.

$R_3P{=}CFX$ (I)

R	Ph	Ph	Ph	Ph	n-Bu	n-Bu	Me_2N	Me_2N
X	H	F	Cl	Br	F	Cl	F	Cl
	(Ia)	(Ib)	(Ic)	(Id)	(Ie)	(If)	(Ig)	(Ih)

These compounds are obtained by different methods and are used without isolation in the "carbonyl olefinating" Wittig reaction. Two cases are then possible.

(1) The phosphorus ylid is generated in the presence of the reagent (carbonyl compound) involved in the subsequent reaction (reaction *in situ*).

(2) The phosphorus ylid is generated and then, without its isolation, the carbonyl compound is added to the reaction mixture ("the olefinating solution").

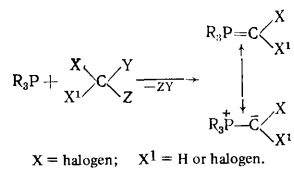
The superiority of a particular method depends not only on the method of generation and stability of the ylid but also on the nature of the reagent, mainly on its reactivity in reactions with the ylids and with the initial compounds from which the ylid is obtained.

Usually, even when the ylids are generated in a preliminary step, there is no certainty that the reaction mixture actually contains the ylid. Although, on subsequent interaction with the reagent, the final products which should have been obtained from the phosphorus ylid are indeed formed, nevertheless in certain cases the ylid is absent from the mixture or is present in very insignificant amounts. This is sometimes confirmed by spectroscopic data (see below), but, even if such evidence is lacking, in their subsequent exposition it will be arbitrarily assumed that the "olefinating solution" does contain the phosphorus ylid.

† In writing this review, the authors used the automated information searching system for the chemistry of organofluorine compounds—AIPS "FTOR" [All-Union Institute of Scientific and Technical Information (VINITI),

II. SYNTHESIS

Regardless of the reaction mechanism, the methods of synthesis of mono- and di-halogenomethylenephosphoranes are based as a rule on the interaction of a tertiary phosphine with some source of a mono- or di-halogenomethylene fragment:

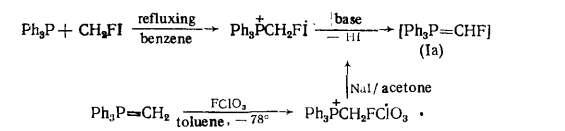


X = halogen; X^1 = H or halogen.

Such sources of halogenomethylenes can be methylene halides, haloforms, carbon tetrahalides, derivatives of halogenoacetic acids, and certain other compounds.

1. Interaction of Tertiary Phosphines with Methylene Halides

Fluoroiodomethane readily alkylates triphenylphosphine to form a stable phosphonium salt[8]. A particularly pure iodide can be obtained by the fluorination of methylenetriphenylphosphorane with subsequent replacement of the anion on treatment with sodium iodide[9]. The dehydroiodination of this salt by BuLi,[8,10] iso-PrNLi,[8] t-BuOK,[11] or the adduct PhLi.LiBr [9] leads to fluoromethylenetriphenylphosphorane (Ia):



(1)

The deuterated ylid $Ph_3P{=}CDF$ has been obtained similarly[12].

2. Interaction of Tertiary Phosphines with Haloforms

The stable fluoroiodomethyltriphenylphosphonium iodide# is formed from triphenylphosphine and fluorodi-iodomethane and is then converted under the influence of the zinc–copper couple into fluoromethylenetriphenylphosphorane (Ia)§ :[8,10]

It may be that in this process the "positively charged" iodine atom is initially attacked by the phosphine with subsequent "anionic exchange" in the phosphonium salt (see below).

§ The phosphorus ylid (Ia) is probably formed as a complex with zinc iodine[8].

$$Ph_3P + CHFI_2 \xrightarrow[CH_2Cl_2]{60^\circ} Ph_3\overset{+}{P}CHFI\ \bar{I} \xrightarrow[DMF]{Zn/Cu,\ 0^\circ} \underset{(Ia)}{[Ph_3P{=}CHF]}\ . \qquad (2)$$

In the presence of strong bases haloforms give rise to dihalogenocarbenes, which can add to a tertiary phosphine to form the corresponding phosphorus ylid. Thus chlorofluoromethylenetriphenylphosphorane (Ic) has been obtained from dichlorofluoromethane and triphenylphosphine in the presence of t-BuOK:[13–16]

$$CHFCl_2 \xrightarrow[-KCl,\ -Me_3COH]{+Me_3COK} [:CFCl] \xrightarrow{+Ph_3P} \underset{(Ic)}{[Ph_3P{=}CFCl]}\ . \qquad (3)$$

It was not possible to obtain by a similar procedure difluoromethylenetriphenylphosphorane (Ib) from chlorodifluoromethane (the initial triphenylphosphine was recovered unchanged)[13]. It has been suggested that the diflurocarbene formed reacts preferentially with t-BuOH and not with Ph_3P. Nor was it possible to obtain analogously difluromethylenetributylphosphorane (Ie) [13] and chlorofluoromethylene-tributylphosphorane (If).[13,14]

3. Interaction of Tertiary Phosphines with Carbon Tetrahalides

The accumulation of electron-accepting halogen atoms in the carbon tetrahalide molecules makes possible the attack by the tertiary phosphine on the "positively charged" halogen. This results in the formation of a halogenophosphonium salt, which can be converted into a trihalogenomethylphosphonium salt by "anion exchange":[17,18]

$$R_3P + CX_4 \rightarrow R_3\overset{+}{P}X\ \bar{C}X_3 \xrightarrow{\bigcirc} R_3\overset{+}{P}CX_3\ \bar{X}\ .$$

In the reaction with mixed fluorine-containing carbon tetrahalides the less electronegative atom of the other halogen is attacked rather than the fluorine atom, which results in the formation of fluorine-containing quaternary phosphonium salts.

Thus the reaction of triphenylphosphine with dibromodifluoromethane yielded the stable bromodifluoromethyltriphenylphosphonium bromide[19,20]. Trichlorofluoromethane does not react with triphenylphosphine under mild conditions, while under more severe conditions a complex mixture of substances is formed[21]. However, the reaction with tris(dimethylamino)phosphine yields readily the stable dichlorofluoromethyltris(dimethylamino)phosphonium chloride[18,22]:

$$Ph_3P + CF_2Br_2 \longrightarrow Ph_3\overset{+}{P}CF_2Br\ \bar{Br}\ ;$$
$$(Me_2N)_3P + CFCl_3 \longrightarrow (Me_2N)_3\overset{+}{P}CFCl_2\bar{Cl}\ .$$

Dehalogenation of phosphonium salts leads to fluorine-containing halogenomethylenephosphoranes. The reaction frequently takes place without the isolation of the phophonium salts, the tertiary phosphine taken in excess serving as the dehalogenating agent. The corresponding ylids (I, b and d) have been obtained in this way from triphenylphosphine and dichlorodifluoromethane[23,24], dibromodifluoromethane[23–29], and tribromofluoromethane[30]:

$$2Ph_3P + CFXY_2 \xrightarrow[\text{diglyme or triglyme;}\ -Ph_3PY_2]{70^\circ} \underset{(I,\ b\ and\ d)}{[Ph_3P{=}CFX]}\ . \qquad (4)$$

X	F	F	Br
Y	Cl	Br	Br

The ylid (Ig) is formed similarly from tris(dimethylamino)phosphine and CF_2Br_2:[26,29]

$$2(Me_2N)_3P + CF_2Br_2 \xrightarrow[\text{triglyme},\ -(Me_2N)_3PBr_2]{20^\circ} \underset{(Ig)}{[(Me_2N)_3P{=}CF_2]}\ . \qquad (5)$$

However, in many instances a multistage synthesis is more convenient: the interaction of equimolar amounts of the phosphine and carbon tetrahalide yields a phosphonium salt, which is then dehalogenated by treatment with a second mole of the phosphine (another tertiary phosphine can be used at this stage). "Olefinating solutions"—sources of difluoromethylenetriphenylphosphorane[20,31], difluoromethylenetris(dimethylamino)phosphorane (Ig),[20,31] and chlorofluoromethylenetris(dimethylamino)phosphorane (Ih) [18,32,33]—have been obtained in this way:

$$R_3\overset{+}{P}CF_2Br\ \bar{Br} + R_3P \xrightarrow[-R_3PBr_2]{} \underset{(I,\ b\ and\ g)}{[R_3P{=}CF_2]}\ ; \qquad (6)$$

$$(Me_2N)_3\overset{+}{P}CFCl_2\ \bar{Cl} + R_3P \xrightarrow[-R_3PCl_2]{} \underset{(Ih)}{[(Me_2N)_3P{=}CFCl]}\ ; \qquad (7)$$

R = Ph or Me_2N.

It must be emphasised that in reality these solutions may not contain phosphorus ylids, although their interaction with carbonyl compounds does yield the products of the Wittig reaction. Thus, after refluxing an acetonitrile solution of equimolar amounts of Ph_3P and bromodifluoromethyltriphenylphosphonium bromide for 6 h, only the initial phosphonium salt was detected by ^{19}F NMR, while difluoromethylenetriphenylphosphorane was not found; nevertheless, on treatment with a carbonyl compound, the Wittig reaction takes place successfully[20]. Evidently the dehalogenation of the phosphonium salt by triphenylphosphine is reversible, the equilibrium being strongly displaced towards the initial compounds. In the presence of a carbonyl compound the phosphorus ylid (Ib) is removed from the reaction, which shifts the equilibrium towards the final products:

$$Ph_3\overset{+}{P}CF_2Br\ \bar{Br} + Ph_3P \rightleftharpoons \underset{(Ib)}{[Ph_3P{=}CF_2]} + Ph_3PBr_2$$
$$\Big| \diagdown C{=}O \qquad (8)$$
$$\downarrow\ \diagup$$
$$\diagdown C{=}CF_2 + Ph_3PO\ .$$

The $(Me_2N)_3\overset{+}{P}CF_2Br\ \bar{Br} + (Me_2N)_3P$ [20] and $(Me_2N)_3\overset{+}{P}CFCl_2\ \bar{Cl} + Ph_3P$ [18] systems behave similarly. On the other hand, when dichlorofluoromethyltris(dimethylamino)phosphonium chloride is acted upon by $(Me_2N)_3P$, an exothermic reaction is observed even in the absence of the third component and the resulting solution does not exhibit an "olefinating" activity¶.[18] Evidently in this case the equilibrium is displaced to the right; in the absence of a carbonyl compound, the resulting ylid (Ih) is removed from the reaction as a result of decomposition[18,33]:

$$(Me_2N)_3\overset{+}{P}CFCl_2\ \bar{Cl} + (Me_2N)_3P \rightarrow \underset{(Ih)}{[(Me_2N)_3P{=}CFCl]} + (Me_2N)_3PCl_2\ .$$
$$\Big|\ \longrightarrow \text{decomposition products}$$

Trihalogenomethylphosphonium salts can be dehalogenated successfully even by metals. Thus the interaction of $CFCl_3$ with triphenylphosphine and zinc in the presence of carbonyl compounds leads to the formation of the products of the Wittig reaction[21,33]. This probably involves the formation of a quasi-complex organometallic compound+, which dissociates into $ZnCl_2$ and the phosphorus ylid (Ic):

$$Ph_3P + CFCl_3 + Zn \xrightarrow[DMF]{60^\circ} \left[\begin{array}{c} ZnCl \\ | \\ Ph_3\overset{+}{P}{-}CFCl\ \bar{Cl} \end{array}\right] \qquad (9)$$
$$\Big\uparrow \qquad \Big\uparrow$$
$$\diagdown C{=}CFCl \xleftarrow[-Ph_3PO]{+\ C{=}O} \underset{(Ic)}{[Ph_3P{=}CFCl]} + ZnCl_2\ .$$

¶ When the reaction is carried out *in situ* (in the presence of a carbonyl compound), the same system gives rise to the products of the Wittig reaction with high yields[18].

+ Similar quasi-complexes of non-fluorinated ylids with mercury(II) chloride are known[34–37].

The formation of the ylid (Ib) is postulated when metals act on a mixture of triphenylphosphine and CF_2Br_2 [29] or on bromodifluoromethyltriphenylphosphonium bromide[28,38]:

$$Ph_3P + CF_2Br_2 + Zn \xrightarrow[AcNMe_2]{100-110^\circ} \underset{(Ib)}{[Ph_3P{=}CF_2]} + ZnBr_2 \quad ; \qquad (10)$$

$$Ph_3\overset{+}{P}CF_2Br\ \bar{B}r \xrightarrow[-HgBr_2]{+Hg} \underset{(Ib)}{[Ph_3P{=}CF_2]} \quad . \qquad (11)$$

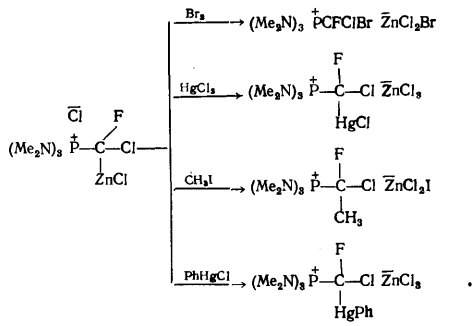
The ylid (Ig) has been obtained similarly[29]:

$$(Me_2N)_3P + CF_2Br_2 + Zn \xrightarrow{AcNMe_2} \underset{(Ig)}{[(Me_2N)_3P{=}CF_2]} + ZnBr_2 \quad . \qquad (12)$$

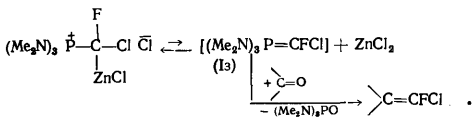
The action of Group IIB metals (zinc, cadmium, and mercury) on dichlorofluoromethyltris(dimethylamino)phosphonium chloride has been studied in particular detail. This entails the formation of an exceptionally stable "olefinating solution" containing a quasi-complex organometallic phosphonium salt#, [32,33] for example:

$$(Me_2N)_3\overset{+}{P}CFCl_2\ \bar{C}l + Zn \xrightarrow[THF]{60^\circ} (Me_2N)_3\overset{+}{P}{-}\underset{ZnCl}{\overset{F}{C}}{-}Cl\ \bar{C}l \quad . \qquad (13)$$

The structure of the quasi-complex salts obtained was confirmed by ^{19}F and ^{31}P NMR and also by chemical reactions[32]:



On treatment with carbonyl compounds, the quasi-complex salts undergo the Wittig reaction, probably as a result of the reversible dissociation into the ylid and a metal salt[32,33]:



In the synthesis of a phosphorus ylid from a trihalogenomethylphosphonium salt the trihalogenomethyl anion can evidently also act as a dehalogenating agent. It has been shown[19,39,40] that trihalogenomethylphosphonium salts serve as convenient sources of trihalogenomethyl anions and dihalogenocarbenes in the presence of alkali metal fluorides, for example:

$$Ph_3\overset{+}{P}CF_2Br\ \bar{B}r \xrightarrow{+\bar{F}} Ph_3PFBr + [\bar{C}F_2Br] \xrightarrow[-Br^-]{} [:CF_2] \quad .$$

In the presence of benzoyl fluoride the product of the Wittig reaction, namely 3-bromotetrafluoro-2-phenylpropene (yield 57%), was obtained in addition to ω-bromo-ω,ω-difluoroacetophenone (yield 9%). [39] It is suggested that this involves the intermediate formation of the ylid (Ib) as a result of the dehalogenation of the phosphonium salt by the anion $\bar{C}F_2Br$:

$$Ph_3\overset{+}{P}CF_2Br\ \bar{B}r \xrightarrow[-Ph_3PFBr]{+KF} [\overset{+}{K}\bar{C}F_2Br] \xrightarrow[-KBr,\ -CF_2Br_2]{+Ph_3\overset{+}{P}CF_2Br\ \bar{B}r} \underset{(Ib)}{[Ph_3P{=}CF_2]} \quad ;$$

$$[\overset{+}{K}\bar{C}F_2Br] + PhCOF \xrightarrow{-KF} PhCOCF_2Br \quad ;$$

$$PhCOCF_2Br + \underset{(Ib)}{[Ph_3P{=}CF_2]} \xrightarrow{-Ph_3PO} \begin{matrix} Ph \\ \diagdown \\ C{=}CF_2 \\ \diagup \\ BrCF_2 \end{matrix} \quad .$$

The "conserving" influence of mercury(II) chloride on non-fluorinated phosphorus ylids is also known[36].

The presence of the phosphorus ylid (Ib) was confirmed by the reaction with trifluoroacetophenone[39]:

$$\underset{(Ib)}{[Ph_3P{=}CF_2]} + PhCOCF_3 \rightarrow \begin{matrix} Ph \\ \diagdown \\ C{=}CF_2 \\ \diagup \\ CF_3 \end{matrix} \ (33\%) \quad .$$

The ylid (Ib) has also been obtained from CF_2Cl_2 under the influence of triphenylphosphine and KF.[15]

The formation of the ylid (Ib) from equimolar amounts of dibromodifluoromethane, triphenylphosphine, and butyllithium was described in 1960 (without experimental details) (the intermediate formation of difluorocarbene was postulated):[41]

$$CF_2Br_2 \xrightarrow[-LiBr]{+BuLi} [:CF_2] \xrightarrow{+Ph_3P} \underset{(Ib)}{[Ph_3P{=}CF_2]} \quad .$$

However, in a later study[13] this result could not be reproduced.

4. The Interaction of Tertiary Phosphines with Derivatives of Trihalogenoacetic Acids

The decarboxylation of trihalogenoacetate salts is frequently used to generate dihalogenocarbenes[40,42]. Decarboxylation in the presence of tertiary phosphines leads to the formation of the corresponding phosphorus ylids. Thus difluoromethylenetriphenylphosphorane has been obtained from lithium[43-46], sodium[43-54], or potassium[44] chlorodifluoroacetate and triphenylphosphine:

$$Ph_3P + ClCF_2COOM \xrightarrow[\text{diglyme, DMF, } N\text{-methylpyrrolidone, etc.}]{80-180^\circ} \underset{(Ib)}{[Ph_3P{=}CF_2]} + MCl + CO_2 \quad ; \qquad (14)$$
$$M = Li, Na \text{ or } K.$$

The analogous reaction with tributylphosphine led to difluoromethylenetributylphosphorane:[51,55]

$$Bu_3P + ClCF_2COONa \xrightarrow[DMF \text{ or } N\text{-methylpyrrolidinone}]{180^\circ} \underset{(Ie)}{[Bu_3P{=}CF_2]} + NaCl + CO_2. \qquad (15)$$

Chlorofluoromethylenetriphenylphosphorane§,[14,16,46,54] bromofluoromethylenetriphenylphosphorane,[30] and chlorofluoromethylenetributylphosphorane[14] have been obtained similarly:

$$Ph_3P + X_2CFCOOM \xrightarrow[triglyme]{80-90^\circ} \underset{(I,\ c \text{ and } d)}{[Ph_3P{=}CFX]} + NaX + CO_2 \quad ; \qquad (16)$$
$$X{=}Cl, Br;\ M{=}Li, Na$$

$$Bu_3P + Cl_2CFCOONa \xrightarrow[triglyme]{85^\circ} \underset{(If)}{[Bu_3P{=}CFCl]} + NaCl + CO_2 \qquad (17)$$

It is sometimes suggested[40,47] that these reactions proceed via the intermediate formation of a dihalogenocarbene:

$$Y{-}\underset{F}{\overset{X}{C}}{-}\overset{O}{\overset{\diagup\!\!\diagdown}{C}}_{OM} \xrightarrow[-MY,\ -CO_2]{\Delta} \left[\begin{matrix} X \\ \diagdown \\ F \end{matrix}\!\!>\!C:\right] \xrightarrow{+R_3P} \left[R_3P{=}C\begin{matrix} X \\ \diagup \\ F \end{matrix}\right] \quad .$$

However, there is important evidence against the "carbene" mechanism. Thus the reaction of chlorofluorocarbene generated from dichlorofluoromethane and t-BuOK with an equimolar mixture of triphenylphosphine and tetramethylethylene leads to almost identical yields of a substituted cyclopropane (II) and the phosphorus ylid (Ic) (the yield of the latter was determined from the results of the Wittig reaction with trifluoroacetophenone):[14,16]

$$CHFCl_2 \xrightarrow[-Me_2COH,\ -KCl]{+Me_2COK} [:CFCl] \xrightarrow{Me_2C{=}CMe_2+Ph_3P} \underset{F\quad Cl}{Me_2C{-}\overset{\diagup\!\!\diagdown}{C}{-}CMe_2} + \underset{(Ic),\ (19\%)}{[Ph_3P{=}CFCl]}$$
(II), (14%)

Consequently tetramethylethylene and triphenylphosphine have comparable reactivities in reactions with dichlorofluorocarbene. However, the decarboxylation of sodium dichlorofluoroacetate in the presence of tetramethylethylene and triphenylphosphine results in the formation of only the phosphorus ylid (Ic) and the cyclopropane (II) is not detected§. The authors[14,16] therefore concluded that the phosphorus ylid is not formed via the halogenocarbene in the present instance. Evidently the trihalogenoacetate behaves in this reaction like carbon tetrahalides (see above), giving rise to the betaine (III) on interaction with phosphine and the betaine is then decarboxylated to give the phosphorus ylid:

$$Ph_3P + Cl_2CFCOONa \xrightarrow{-NaCl} \underset{(III)}{[Ph_3\overset{+}{P}CFCl\overline{CO}O]} \xrightarrow{-CO_2} \underset{(Ic)}{[Ph_3P{=}CFCl]} .$$

Analogous evidence in support of the formation of the betaine $Ph_3\overset{+}{P}CF_2\overline{CO}O$ when difluoromethylenetriphenylphosphorane (Ib) is generated has been adduced by other workers[43]. It has also been shown that the presence of triphenylphosphine accelerated the decarboxylation of sodium chlorodifluoroacetate[43].

Naturally, the mode of reaction should depend on the nucleophilic activity of the tertiary phosphine and on the nature of the halogen atoms in the trihalogenoacetate. The latter affects both the ease of the nucleophilic attack by the phosphine on the halogen atom and the ease of decarboxylation. Nor can one rule out the possibility that in various specific instances the reaction mechanism is different (the "carbene" or "phosphobetaine" mechanism).

In the synthesis of difluoromethylenetriphenylphosphorane (Ib) it is also possible to use trimethyltin trifluoroacetate as the initial trihalogenoacetate[56]:

$$Ph_3P + CF_3COOSnMe_3 \xrightarrow[-Me_3SnF,\ -CO_2]{150^\circ,\ NaI} \underset{(Ib)}{[Ph_3P{=}CF_2]} .$$

The interaction of methyl trihalogenoacetates with a tertiary phosphine in the presence of nucleophiles capable of demethylating esters is a variety of the method of synthesis of fluoromethylenephosphoranes described. Thus difluoromethylenetriphenylphosphorane is formed when methyl chlorodifluoroacetate is acted upon by triphenylphosphine and the complex of LiCl with hexamethylphosphoramide (HMP):[57]

$$Ph_3P + ClCF_2COOMe \xrightarrow[\sim 80^\circ,\ \text{triglyme}]{LiCl\cdot 2(Me_2N)_3PO} \underset{(Ib)}{[Ph_3P{=}CF_2]} . \qquad (18)$$

The ylid (Ib) could be formed via two pathways: via the difluorocarbene (a) or via the phosphonium salt (IV)¶ and the phosphobetaine (V)† (b):

a) $ClCF_2COOMe \xrightarrow[-MeCl]{+LiCl} ClCF_2COOLi \xrightarrow[-LiCl,\ -CO_2]{} [:CF_2] \xrightarrow{+Ph_3P} \underset{(Ib)}{[Ph_3P{=}CF_2]}$

b) $Ph_3P + ClCF_2COOMe \rightarrow \underset{(IV)}{[Ph_3\overset{+}{P}CF_2COOMe\overline{Cl}]} \xrightarrow[-MeCl]{(LiCl)}$

$\rightarrow \underset{(V)}{[Ph_3\overset{+}{P}CF_2\overline{CO}O]} \xrightarrow{-CO_2} \underset{(Ib)}{[Ph_3P{=}CF_2]}$

§ In the absence of triphenylphosphine the cyclopropane (II) was obtained in 37% yield[14,16].

¶ It has been shown[58,59] that, on heating (90–120 °C in DMF), the salt $Ph_3\overset{+}{P}CH_2COOMe\overline{Br}$ decomposes into MeBr, CO_2, and the ylid $Ph_3P{=}CH_2$.

† From the point of view of stoichiometry, the reaction should take place, in principle, in the presence of catalytic amounts of LiCl regardless of its mechanism. However, an excess of the complex of LiCl with HMP was used[57], evidently in order to increase the rate of reaction [the resulting ylid (Ib) was used in the Wittig reaction *in situ*].

Since the presence of triphenylphosphine does not accelerate the decomposition of methyl chlorodifluoroacetate, the "carbene" mechanism (a) is more probable[57].

The chlorofluoro-substituted phosphorus ylid (Ic) has been obtained from methyl dichlorofluoroacetate and triphenylphosphine in the presence of NaH and methanol under mild conditions, possibly via chlorofluorocarbene[60]:

$$Ph_3P + Cl_2CFCOOMe \xrightarrow[\substack{25-30^\circ;\\ \text{heptane or}\\ \text{benzene}}]{NaH/MeOH} \underset{(Ic)}{[Ph_3P{=}CFCl]} . \qquad (19)$$

5. Other Methods of Synthesising Fluorine-Containing Halogenomethylenephosphoranes

On interaction with triphenylphosphine, the usual source of chlorofluorocarbene—dichlorofluoromethylphenylmercury—gives rise to chlorofluoromethylenetriphenylphosphorane:[15]

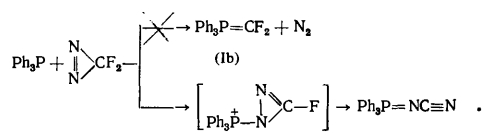
$$Ph_3P + PhHgCFCl_2 \xrightarrow[\text{xylene}]{80^\circ} \underset{(Ic)}{[Ph_3P{=}CFCl]} + PhHgCl . \qquad (20)$$

It has been claimed[61] that difluoromethylenetriphenylphosphorane is formed when trifluoronitrosomethane interacts with ammonia and triphenylphosphine. Difluorodiazomethane is then postulated as an intermediate:

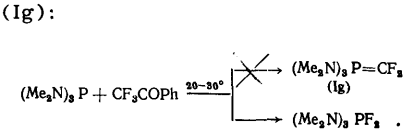
$$CF_3NO \xrightarrow[-H_2O]{+NH_3} [CF_3N{=}NH] \xrightarrow[-NH_4F]{+NH_3} [\overline{C}F_2{-}\overset{+}{N}{\equiv}N] \xrightarrow[-N_2]{+Ph_3P} \underset{(Ib)}{[Ph_3P{=}CF_2]} .$$

However, no evidence has been produced in support of the formation of the ylid (Ib).[61]

The ylid (Ib) cannot be obtained from difluorodiazirine (difluorocyclodiazomethane) and triphenylphosphine[62]:

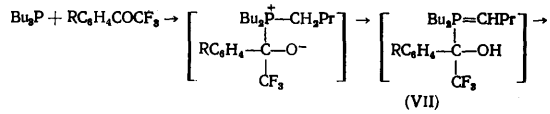


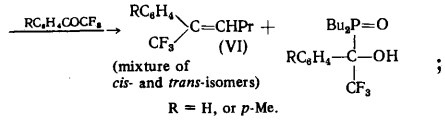
Mark[63] reported the synthesis of difluoromethylenetris-(dimethylamino)phosphorane and its ethyl analogue $(Et_2N)_3P{=}CF_2$ by the reaction of the corresponding phosphorus acid triamides [tris(dialkylamino)phosphines] with trifluoroacetophenone. These phosphorus ylids have been described[63] as stable distillable liquids. However, it was shown later[64] that in fact the reaction products are not phosphorus ylids but tris(dialkylamino)difluorophosphoranes, whose structure was demonstrated rigorously by spectroscopic data and by specific synthesis[62,64,65]. The properties of tris(dimethylamino)-difluorophosphorane agree fully with those of the compound described by Mark[63], who incorrectly attributed to it the structure (Ig):



Only traces of the ylid (Ig) were detected in the reaction medium by mass spectrometry[64].

Tributylphosphine reacts differently with difluoroacetophenone (and *p*-methyltrifluoroacetophenone); the reaction yields the olefins (VI) probably via the phosphorus ylids (VII):[66]





Other trialkylphosphines react similarly[66].

III. PROPERTIES

As already mentioned, fluorine-containing mono- and di-halogenomethylenephosphoranes (I, a–h) have not been isolated in a pure state#. When different methods of synthesis are used, the reaction mixtures frequently contain different compounds, which are in principle capable of interacting both with the phosphorus ylid (reversibly or irreversibly) and with other reagents. All this causes extreme difficulties in the determination of reliable data on the comparative stabilities and reactivities of fluorine-containing halogenomethylenephosphoranes, despite the extensive experimental results which have been accumulated. However, since these compounds have already assumed a fairly considerable importance and are widely used in the synthesis of fluorine-containing olefins by the Wittig reaction, it is necessary to describe the available data concerning their stabilities. In the first place we shall consider the use of fluorine-containing halogenomethylenephosphoranes in the Wittig reaction.

1. Stability of Fluorine-Containing Halogenomethylenephosphoranes

When the stabilities of compounds (I) are considered, one must not overlook the fact that in practice one is not dealing with a phosphorane as such but with a reaction mixture containing different components. In each case attention must therefore be directed not only to the nature of the ylid but also to the method of its synthesis.

(*a*) *Fluoromethylenetriphenylphosphorane* $Ph_3P=CHF$ (*Ia*). The phosphorus ylid (Ia), obtained in the form of a lemon-yellow solution in tetrahydrofuran (THF) on dehydroiodination of a phosphonium salt by PhLi [(Eqn.(1)], is readily attacked by nucleophiles and decomposes. In its synthesis it is necessary to add slowly, with very thorough stirring, a solution of PhLi to fluoromethyltriphenylphosphonium iodide and to maintain a fairly low temperature (<–50 °C) to avoid self-condensation§ [9] (see also Vanderhaar et al.[30]). Nevertheless this ylid can be generated in solution in the absence of a carbonyl compound and then used in the Wittig reaction[9]. The use of BuLi in a mixture of THF and hexane also leads to a relatively stable solution of the ylid (Ia) (it does not decompose at 0 °C for 40 min but does decompose at 28 °C).[8]

The "olefinating solution", obtained by the dehalogenation of fluoroiodomethyltriphenylphosphonium iodide with the zinc–copper couple in dimethylformamide (DMF) [Eqn.(2)], apparently contains the complex $Ph_3\overset{+}{P}CHFZnI\ \bar{I}$ and not the free ylid (Ia). The solution is relatively unstable—after 90 min at 0 °C it loses almost completely its "olefinating" capacity and is therefore used in the Wittig reaction *in situ*[8].

(*b*) *Difluoromethylenetriphenylphosphorane* $Ph_3P=CF_2$ (*Ib*). Under the conditions of its synthesis by the "halogenoacetate" method [Eqn.(14)], the ylid (Ib) is unstable and can be used in the Wittig reaction only *in situ* in solvents such as diglyme, DMF, and *N*-methylpyrrolidinone. The attempts to use dimethyl sulphoxide as the solvent were unsuccessful, evidently as a result of the interaction of the ylid (Ib) with Me_2SO (dimethyl sulphide was isolated from the reaction product in 84% yield)[43].

When triphenylphosphine reacts with dibromodifluoromethane or bromodifluoromethyltriphenylphosphonium bromide in diglyme, triglyme, or acetonitrile [Eqns.(4) and (6)], stable "olefinating solutions" are formed (they do not decompose in 60 h at 70 °C).[20,26] Their stability can be explained by the reversibility of the formation of the ylid (Ib) and the appreciable shift of the equilibrium [Eqn.(8)] to the left. However, in DMF it is impossible to obtain a stable solution—probably as a consequence of the interaction of the solvent with dibromotriphenylphosphorane Ph_3PBr_2, which shifts the equilibrium to the right[20].

(*c*) *Chlorofluoromethylenetriphenylphosphorane* $Ph_3P=CFCl$ (*Ic*). In contrast to the difluoroylid (Ib), the chlorofluoroylid (Ic) is comparatively stable under the conditions of its synthesis from triphenylphosphine and sodium dichlorofluoroacetate [Eqn.(16)]. After the evolution of CO_2 (after heating for several hours at 80–90 °C in triglyme), a solution with "olefinating" activity was obtained; however, the yields in the Wittig reaction were nevertheless higher when the ylid was employed *in situ*.[14,16]

When chlorofluoromethylenetriphenylphosphorane was generated under mild conditions from methyl dichlorofluoroacetate, Ph_3P, and NaH [Eqn.(19)][60] or from $CHFCl_2$, Ph_3P, and t-BuOK [Eqn.(3)],[13,14,16] relatively stable "olefinating" solutions are also formed.

(*d*) *Bromofluoromethylenetriphenylphosphorane* $Ph_3P=CFBr$ (*Id*). The solution obtained by the reaction of triphenylphosphine with tribromofluoromethane in diglyme or triglyme at 70 °C [Eqn.(4)] does not lose its "olefinating" capacity after 21 h at 37 °C.[30]

(*e*) *Tributyldifluoromethylenephosphorane* $Bu_3P=CF_2$ (*Ie*) *and tributylchlorofluoromethylenephosphorane* $Bu_3P=CFCl$ (*If*). The tributyl-substituted ylids (Ie) and (If) are apparently less stable than the corresponding triphenyl ylids (Ib) and (Ic).[13,14,16] Tributyldifluoromethylenephosphorane[51] and tributylchlorofluoromethylenephosphorane[14] can be generated by the "halogenoacetate" method [Eqns.(15) and (17)] and used in the Wittig reaction *in situ*; however, the attempts to obtain them from a haloform, a phosphine, and t-BuOK [as in Eqn.(3)] proved unsuccessful[13,14,16]. It has been suggested[13] that the ylid (If) reacts with t-BuOH under the reaction conditions.

(*f*) *Difluoromethylenetris(dimethylamino)phosphorane* $(Me_2N)_3P=CF_2$ (*Ig*). The "olefinating" solutions which behave as sources of the ylid (Ig) are prepared by treating dibromodifluoromethane [Eqn.(5)][26] or bromodifluoromethyltris(dimethylamino)phosphonium bromide [Eqn.(6)] with tris(dimethylamino)phosphine in triglyme[20,31]¶. These solutions are stable at room temperature (they hardly decompose after 300 h),[26] probably as a consequence of the establishment of a dynamic equilibrium, which ensures the virtual absence of the ylid from the mixture[20] (see above).

Dichloromethylenetriphenylphosphorane $Ph_3P=CCl_2$ has been isolated in the form of a yellow powder; its structure was demonstrated spectroscopically[67].

§ Schlosser and Zimmermann[9] do not give any details.

¶ The report of the isolation of the ylid (Ig) in a pure form[63] was erroneous (see above).

(g) Chlorofluoromethylenetris(dimethylamino)phosphorane $(Me_2N)_3P=CFCl$ *(Ih).* When Ph_3P reacts with dichlorofluoromethyltris(dimethylamino)phosphonium chloride in benzonitrile [Eqn.(7)], a very stable "olefinating" solution is formed (it does not decompose after 500 h at room temperature or after 24 h at 60 °C). On the other hand, if tris(dimethylamino)phosphine is used instead of triphenylphosphine, the above system can be used in the Wittig reaction only *in situ*[18]. These results can be explained by the different equilibrium positions[18,33] (see above).

The quasi-complex salts obtained when dichlorofluoromethyltris(dimethylamino)phosphonium chloride is acted upon by metals [Eqn.(13)] are usually very stable[32,33]. The organozinc phosphonium salt does not decompose in THF after 10 h at 60 °C or after 30 days at room temperature; the solution in PhCN is less stable (2 h at 60 °C). The analogous cadmium derivative decomposes after 2 h at 60 °C in THF and after 1 h in PhCN. The mercury derivative is particularly stable (it does not decompose after 83 h at 60 °C in PhCN).

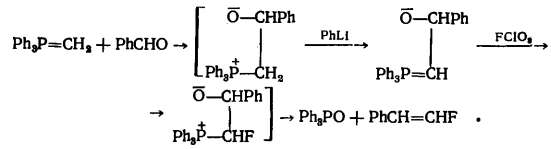
2. Fluorine-Containing Halogenomethylenephosphoranes in the Wittig Reaction. The Synthesis of Fluoro-olefins

The synthesis of olefins by the Wittig reaction is the principal application of phosphorus ylids[1,2,4,6]. Fluorine-containing halogenomethylenephosphoranes are also widely used to synthesise fluoro-olefins from carbonyl compounds†.

The important role of fluoro-olefins as "key" compounds in organofluorine chemistry is known. Despite the abundance of methods for the synthesis of fluoro-olefins, the expansion of this field with the aid of the Wittig reaction is important.

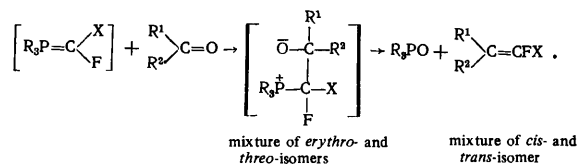
The ease of the Wittig reaction depends on the nucleophilic properties of the ylid and the electrophilic properties of the carbonyl compound[1,2]. The introduction of a halogen into methylenephosphorane apparently reduces somewhat its nucleophilic reactivity[4], but it is nevertheless sufficient for interaction with aldehydes and also with ketones having electron-accepting fluoroalkyl groups. The conversion of inactive ketones into olefins is achieved with much more difficulty. The method of enhancing the nucleophilic properties of the ylid based on the introduction of electron-donating groups at the phosphorus atom has been used recently on an increasing scale. The employment of tris(dimethylamino)-phosphoranes $(Me_2N)_3P=CFX$ instead of triphenyl derivatives $Ph_3P=CFX$ makes it possible in a number of instances to convert into olefins also inactivated ketones. Equilibrium mixtures containing the phosphorus ylid in very low amounts are frequently used in the Wittig reaction instead of the "pure" halogenomethylenephosphoranes; only under the influence of a carbonyl compound does the ylid react with the latter and the equilibrium is displaced to the right. Such "olefinating" systems include mixtures of trihalogenomethylphosphonium salts with tertiary phosphines (see above) and quasi-complex organometallic phosphonium salts (see above). This form of the ylid usually ensures the stability of the "olefinating" agent, but reduces its reactivity.

Apart from using fluorine-containing phosphorus ylids in order to obtain fluoro-olefins, it is possible to apply also another procedure, which likewise involves the Wittig reaction. This is the SCOOPY method (α-substitution plus carbonyl olefination via β-oxido-phosphorus ylids)[4,71-73]. The method is based on the conversion with the aid of a strong base of the phosphobetaine formed from the phosphorus ylid and the carbonyl compound into a "β-oxido-phosphorus ylid", which reacts with an electrophile to form a new α-substituted phosphobetaine; the decomposition of the latter leads to a substituted olefin. For example, when "β-oxido-phosphorus ylid" is fluorinated with subsequent decomposition of the α-fluorophosphobetaine, an α-fluoro-olefin is formed[71]:



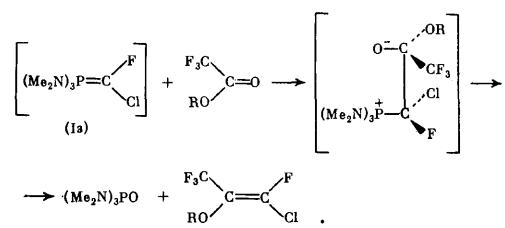
Thus, in terms of its results, this reaction is equivalent to the Wittig reaction with fluoromethylenephosphorane.

In reactions of monofluoro-, chlorofluoro-, and bromofluoro-methylenephosphoranes with aldehydes and asymmetric ketones there is a possibility of the *cis-trans* isomerism of the final products#. In contrast to the reactions with non-fluorinated active phosphorus ylids, which are frequently stereoselective[2,3,11,73,74], the reactions with halogenomethylenephosphoranes as a rule yield *cis*- and *trans*-olefins in approximately equal amounts[8,9,11,12,14-16,18,21,30,32,60]:



mixture of *erythro*- and *threo*-isomers — mixture of *cis*- and *trans*-isomer

Only the interaction of chlorofluoromethylenetris(dimethylamino)phosphorane with fluorocarboxylate esters proved to be stereoselective—mainly the *Z*-isomers of alkylpolyfluoroalkenyl esters are then formed[18,32] (see below). Evidently only one of the diastereoisomeric intermediate phosphobetaines is formed under these conditions:



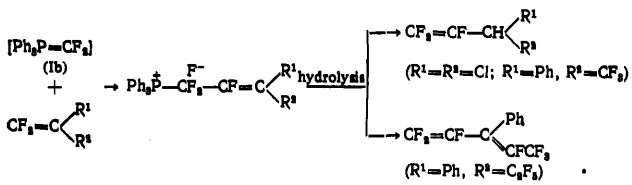
(Ia)

The synthetic applications of fluorine-containing halogenomethylenephosphoranes are virtually limited to the Wittig reaction. However, there are data (without experimental details)[38] showing that difluoromethylenetriphenylphosphorane, generated by treating bromodifluoromethyltriphenylphosphonium bromide with mercury [Eqn.(11)], reacts with fluoro-olefins to form allylphosphonium salts—the products of the "vinyl" substitution of the fluorine atom in the olefin.

† Fluoro-olefins are also obtained from phosphorus ylids without fluorine and from fluorocarbonyl compounds[68,69]. An interesting pathway leading to fluoro-olefins arises from the reaction of phosphorus ylids with halogenocarbenes[70]: $Ph_3P=CR^1R^2 + :CF_2 \rightarrow Ph_3P + R^1R^2C=CF_2$.

For the mechanism and stereochemistry of the Wittig reaction, see Refs.2–4 and 73–77.

Hydrolysis of these salts leads to the cleavage of the C–P bond and the formation of olefins or dienes:



Methods for the introduction of the =CHF, $=CF_2$, =CFCl, and =CFBr groups with the aid of the Wittig reaction are examined below:

(*a*) *The introduction of the =CHF group.* α-Fluoro-α-hydro-olefins are obtained from fluoromethylenetriphenylphosphorane, generated either by the dehydrohalogenation of a fluoromethyltriphenylphosphonium salt [Eqn.(1)][8,9,11] or by the dehalogenation of a fluoroiodomethyltriphenylphosphonium salt [Eqn.(2)].[8,10] The reaction involves aldehydes (aliphatic and aromatic)[8–11] and ketones (activated and non-activated)[8,10]:

$$[Ph_3P{=}CHF] + RCHO \rightarrow RCH{=}CHF + Ph_3PO$$
(Ia) — mixture of *cis*- and *trans*-isomers (~ 1 : 1)

R = n-C_5H_{11}, n-C_6H_{13}, Ph, *m*-ClC_6H_4, or *m*-$CF_3C_6H_4$ (~ 20 °C, THF or CH_2Cl_2, yield 25–65%);
R = n-C_6H_{13}, Ph, or C_6F_5 (0 °C, DMF, yield 52–65%);

$$[Ph_3P{=}CHF] + \underset{R^1}{\overset{R}{\rangle}}C{=}O \rightarrow \underset{R^1}{\overset{R}{\rangle}}C{=}CHF + Ph_3PO$$
(Ia)

$RR^1 = -(CH_2)_5-$; Ph, Me (~20 °C, THF/hexane, yield 48–69%); RR^1 = $PhCF_3$ (0 °C, DMF, yield 80%).

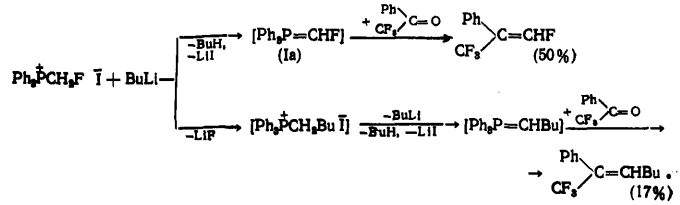
A deuterated olefin was obtained similarly (yield 48%):[12]

$$[Ph_3P{=}CDF] + PhCHO \xrightarrow[THF]{20^\circ} PhCH{=}CDF .$$

A 17-fluoromethylene-substituted steroid has been formed from the 2-tetrahydropyranyl ether of 3β-hydroxo-17-oxo-5-androstene (yield 16%).[9] The attempts to obtain by this method fluoromethylene-substituted sugars from the corresponding ketones were unsuccessful[15].

In the case of non-activated ketones best results are obtained by generating the ylid (Ia) from a fluoromethylphosphonium salt [Eqn.(1)] and, in the case of aldehydes and trifluoroacetophenone, from a fluoroiodomethylphosphonium salt [Eqn.(2)] using the ylid *in situ* in a DMF solution[8].

When BuLi is used to dehydrohalogenate a phosphonium salt in accordance with Eqn.(1), the resulting "olefinating" solution is made to react with a carbonyl compound and the mixture is then treated with potassium t-butoxide; without such treatment, the yields of olefins are reduced[8]. It has been suggested that the betaines produced as intermediates in the Wittig reaction form stable complexes with lithium salts, which hinders their cyclisation to oxaphosphetans preceding the cleavage to the final product—an olefin and a phosphine oxide (cf. Schlosser and Christmann[78]). However, in certain cases the yield of the product of the Wittig reaction is reduced as a consequence of its interaction with t-BuOK. Another cause of the reduced yield of the fluoro-olefin is the formation of a butylolefin as a side product[8]:



Since it has been shown that the entire butyl-lithium is consumed before the ketone is added, the source of the butyl group in the side reaction is apparently a butyl-substituted phosphorus ylid.

It must be emphasised that in many cases it is more convenient to synthesise α-hydrofluoro-olefins by the selective reduction of the corresponding α,α-difluoro-olefins[29] or α-chloro-α-fluoro-olefins[15] and not by the Wittig reaction.

(*b*) *The introduction of the* $=CF_2$ *group.* α,α-Difluoro-olefins are usually obtained from difluoromethylenetriphenylphosphorane, but tributyldifluoromethylenephosphorane and difluoromethylenetris(dimethylamino)phosphorane are also used.

Difluoromethylenetriphenylphosphorane is usually generated from $ClCF_2COONa$ and Ph_3P [Eqn.(14)][43–54] and is used *in situ* in the Wittig reaction§. This ylid gives rise to satisfactory yields of α,α-difluoro-olefins on reaction with aldehydes[45,47,50] and activated ketones[43,52]:

$$[Ph_3P{=}CF_2] + RCHO \xrightarrow[N\text{-methylpyrrolidinone, etc}]{80-180^\circ} RCH{=}CF_2 + Ph_3PO ;$$
(Ib) — (50–75%)

R = n-C_6H_{13}, Ph, *p*-$MeOC_6H_4$, or *p*-FC_6H_4, ;

$$[Ph_3P{=}CF_2] + \underset{CF_3}{\overset{R}{\rangle}}C{=}O \xrightarrow[\text{diglyme, DMF; etc.}]{75-148^\circ} \underset{CF_3}{\overset{R}{\rangle}}C{=}CF_2 + Ph_3PO ;$$
(Ib) — (60–85%)

R = n-Bu, C_6H_{11}, $PhCH_2$, Ph¶, *p*-FC_6H_4, *p*-MeC_6H_4 or *p*-$MeOC_6H_4$.

In the reaction with *p*-dimethylamino-ω,ω,ω-trifluoroacetophenone the yield of the olefin *p*-$Me_2NC_6H_4C(CF_3){=}CF_2$ is only 16%.[43]

In many instances the products include, apart from α,α-difluoro-olefins, the products of their reactions in the presence of the F^- anion†. The use of lithium chlorodifluoroacetate instead of the sodium salt usually suppresses these reactions, since LiF is less reactive with respect to fluoro-olefins than NaF.[43,44] Thus the olefin *p*-$ClC_6H_4C(CF_3){=}CF_2$ (yield 32%) and the product of the addition of hydrogen fluoride *p*-$ClC_6H_4CH(CF_3)_2$ (yield 37%) have been obtained from *p*-chlorotrifluoroacetophenone, $ClCF_2COONa$, and Ph_3P in diglyme; in the reaction with the lithium salt in DMF the yield of the olefin increases to 64%.[43]

In the reaction with ketones containing perfluoroalkyl groups the isomerisation of the terminal fluoro-olefin to an internal fluoro-olefin is frequently observed[44], for example:

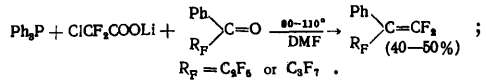
$$[Ph_3P{=}CF_2] + \underset{CF_3CF_2}{\overset{Ph}{\rangle}}C{=}O \xrightarrow{-Ph_3PO} \underset{CF_3CF_2}{\overset{Ph}{\rangle}}C{=}CF_2 \xrightarrow{400^\circ F} \underset{CF_3CF}{\overset{Ph}{\rangle}}C{-}CF_3 .$$
(Ib)

§ A mixture of a phosphine, an acid salt, and a carbonyl compound is heated in the solvent until the evolution of CO_2 ceases. When large amounts of the reactants are used, it is more convenient to add the salt solution dropwise to a heated solution of Ph_3P and the carbon compound[43,50]. When a lithium salt is used, the yield of the α,α-difluoro-olefin is increased[45].

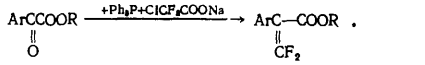
¶ The best yield of 2-phenylpentafluoropropene (80%) was obtained when the ylid (Ib) was generated from methyl chlorodifluoroacetate [Eqn.(18)].[57]

† It has been suggested[43,44] that the F^- anion is generated on decomposition of the ylid (Ib) or directly by the decarboxylation of $ClCF_2COOM$. The yield of the olefin *p*-$O_2NC_6H_4CH{=}CF_2$, formed from *p*-nitrobenzaldehyde, in only 2%, while the yield of the addition product HF–*p*-$O_2NC_6H_4CH_2CF_3$ is ~20%.[50]

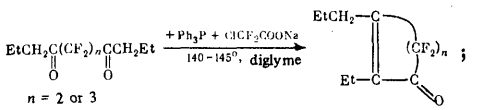
However, the use of a lithium salt suppresses the isomerisation[43,44]:



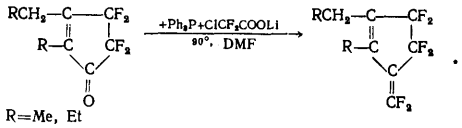
In contrast to aldehydes and activated ketones, cyclohexanone[51] and acetophenone[52] do not react with difluoromethylenetriphenylphosphorane, evidently owing to the insufficiently pronounced electrophilic properties of the carbonyl carbon[43]. The esters of aromatic α-ketoacids enter into the Wittig reaction, forming the esters of α-aryl-β,β-difluoroacrylic acids[54,79,80]:



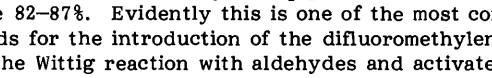
When the ylid (Ib) was generated by the "halogenoacetate" method, it was not possible to achieve the Wittig reaction with the diketones $PhCO(CF_2)_nCOPh$ (n = 2 or 3).[46] In the reaction with the analogous dipropyl-substituted diketones the ylid (Ib) induces their cyclisation to unsaturated ketones[46]:



Fluorocyclopentorones undergon the Wittig reaction (in contrast to the corresponding cyclohexanones) and give low yields of difluoromethylenecyclopentenes[46]:



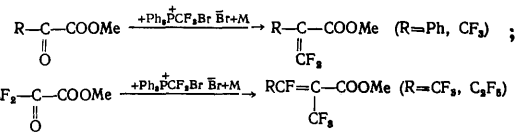
When another method of synthesis of the ylid (Ib) is used, namely from Ph_3P and CF_2Br_2 [Eqn.(4)], it is possible to involve also diketones in the Wittig reaction[28]:



This method of generation of the ylid (Ib) has been used successfully in the reactions with PhCHO,[23,24,29] PhCH=CHCHO,[29] $PhCOCF_3$,[20,25] p-$ClC_6H_4COCF_3$,[25] $PhCOC_2F_5$,[25] m-$BrC_6H_4COCF_3$,[25] and m-$BrC_6H_4COC_2F_5$;[25] the yields of olefins are 82–87%. Evidently this is one of the most convenient methods for the introduction of the difluoromethylene group in the Wittig reaction with aldehydes and activated ketones. However, particularly severe requirements are then imposed on the dryness of solvents[29].

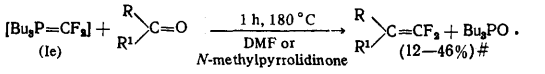
In the reaction with aldehydes the method of generation of difluoromethylenetriphenylphosphorane from Ph_3P, CF_2Br_2, and zinc [Eqn.(10)] is even more convenient. α,α-Difluoro-olefins are readily obtained by this procedure from n-C_6H_{13}.CHO, n-$C_{10}H_{21}CHO$, and PhCHO (yields ~80%), as well as PhCH=CHCHO (yield 33%);[29] there is then no need for especially thorough drying of solvents. In the reaction with PhCOMe the yield of difluoro-olefin does not exceed 5%.

The esters of α-substituted perfluoroacrylic acids and their isomerisation products have been obtained by the interaction of the esters of α-ketoacids with bromodifluoromethyltriphenylphosphonium bromide and a metal[28]:



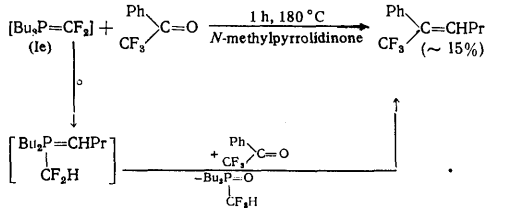
Difluoromethylene-substituted sugars have been prepared by treating the corresponding oxo-derivatives with triphenylphosphine, dichlorofluoromethane, and KF.[15] The intermediate formation of the ylid (Ib) in the reaction of bromodifluoromethyltriphenylphosphonium bromide with KF and PhCOF was described above.

Since difluoromethylenetriphenylphosphorane does not as a rule enter into the Wittig reaction with non-activated ketones, the corresponding difluoro-olefins must be synthesised using other more active difluoromethylenephosphoranes. The use of tributyldifluoromethylenephosphorane, generated by the "halogenoacetate" method [Eqn.(15)], for this purpose has been described[51,55]:



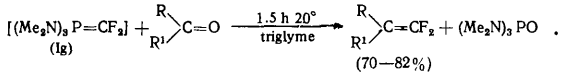
The reaction is carried out *in situ* with cyclohexanone, benzophenone, and methylketones MeCOR (R = C_5H_{11}, Ph, 2-furyl, or 2-thienyl). In the reaction with heptanal the yield of the olefin n-$C_6H_{13}CH=CF_2$ is only 7%.[51]

In the interaction with trifluoroacetophenone the carbonyl oxygen is replaced by the butylidene group and not the difluoromethylene group, probably as a consequence of the isomerisation of the ylid (Ie):[43,51]



α,α-Difluoro-olefins could not be obtained either by treating phenyl α-pyridyl ketone, p-benzoquinone, hexachloroacetone, and camphor with tributyldifluoromethylenephosphorane[51].

The most convenient source of the difluoromethylene group in the Wittig reaction with non-activated ketones is evidently difluoromethylenetris(dimethylamino)phosphorane generated from dibromodifluoromethane [Eqns.(5) and (6)].[20,26,29,31]§ The enhanced nucleophilic activity of the ylid (Ig), induced by the electron-donating influence of the dimethylamino-groups, ensures high yields of difluoro-olefins from cyclohexanone, diethyl ketone, acetophenone, and propiophenone[20,26]:



The reaction can be carried out *in situ* or with preliminary generation of the "olefinating solution"[20,26]. However, one should use very thoroughly dried solvents[29].

This method is evidently unsuitable for the Wittig reaction with activated fluorine-containing ketones, because fluoroketones react with tris(dimethylamino)phosphine[64].

The ylid (Ig), generated from $(Me_2N)_3P$, CF_2Br_2 and zinc [Eqn.(12)] has been used successfully in reactions with aldehydes. The yield of 1,1-difluoro-oct-1-ene from n-$C_6H_{13}CHO$ is 77%. β,β-Difluoro-α-methylstyrene is formed in ~40% yield from acetophenone[29]. Careful drying of the solvent is not required.

#In a later communication it is stated[26] that the yields do not exceed 10%.

§For a description of the equilibrium in the $(Me_2N)_3\overset{+}{P}CF_2Br\ \overline{Br} + (Me_2N)_3P \rightleftharpoons (Me_2N)_3P=CF_2 + (Me_2N)_3PBr_2$ system, see above.

(c) *The introduction of the group =CFCl.* Chlorofluoromethylenetriphenylphosphorane and chlorofluoromethylenetris(dimethylamino)phosphorane are widely used in the synthesis of α-chloro-α-fluoro-olefins by the Wittig reaction.

When the ylid (Ic) is generated by the "halogenoacetate" method [Eqn.(16)][14,16] or its modification Eqn.(19)], aldehydes and activated ketones are successfully "olefinated" with formation of a mixture of *cis*- and *trans*-isomers of chlorofluoro-olefins (in proportions of ~1 : 1):

$$[Ph_3P{=}CFCl] + RCHO \xrightarrow[\text{ether}]{\text{triglyme or petroleum}} RCH{=}CFCl + Ph_3PO \quad (25\text{—}63\%)$$
(Ic)

R = n-Bu, Ph, *p*-ClC_6H_4, *p*-$MeOC_6H_4$, or *o*-$MeOC_6H_4$;

$$[Ph_3P{=}CFCl] + \underset{CF_3}{\overset{R}{\diagdown}}C{=}O \xrightarrow[\text{triglyme}]{90^\circ} \underset{CF_3}{\overset{R}{\diagdown}}C{=}CFCl + Ph_3PO \quad (30\text{—}70\%)$$
(Ic)

R=n-Bu, C_6H_{11}, $PhCH_2$, Ph, *p*-ClC_6H_4, *p*-FC_6H_4, *p*-MeC_6H_4, *p*-$MeOC_6H_4$;

$$[Ph_3P{=}CFCl] + \underset{R_F}{\overset{Ph}{\diagdown}}C{=}O \xrightarrow[\text{triglyme}]{90^\circ} \underset{R_F}{\overset{Ph}{\diagdown}}C{=}CFCl + Ph_3PO \quad (41\text{—}42\%)$$
(Ic)

R_F=C_3F_8, n-C_3F_7.

Non-activated ketones enter into this reaction with difficulty, so that there is sufficient time for the decomposition of the ylid (Ic).[14,16] It has been shown[60] that the reactivity of carbonyl compounds in relation to chlorofluoromethylenetriphenylphosphorane decreases in the sequence *p*-ClC_6H_4. .CHO > PhCHO > $PhCOCF_3$ > PhCOMe. Benzophenone could not be "olefinated" and the reactions with acetophenone, cyclopentanone, and cyclohexanone gave only small yields of the corresponding olefins[14,16,60]. Nor was it possible to make 1,2-dialkylhexafluorocyclohex-3-enones to undergo the reaction[46].

The esters of α-aryl-β-chloro-β-fluoroacrylic acids were obtained from the esters of aromatic α-ketoacids[54]:

$$Ar{-}\underset{\underset{O}{\|}}{C}{-}COOR \xrightarrow{+Ph_3P+CCl_2FCOONa} Ar{-}\underset{\underset{CFCl}{\|}}{C}{-}COOR .$$

When the ylid (Ic) is generated from Ph_3P, $CHFCl_2$, and t-BuOK [Eqn.(3)], which requires milder conditions than the synthesis by the "halogenoacetate" method, chlorofluoromethylenecyclopentane is formed from cyclopentanone in 27% yield[14,16]. The report that benzophenone was made to undergo the reaction[13] was not confirmed[14,16]. Olefins have also been obtained by this method from benzaldehyde and from activated ketones[14,16]:

$$[Ph_3P{=}CFCl] + \underset{XCF_2}{\overset{Ph}{\diagdown}}C{=}O \xrightarrow[\text{heptane}]{20^\circ} \underset{XCF_2}{\overset{Ph}{\diagdown}}C{=}CFCl + Ph_3PO \quad (30\text{—}50\%)$$
(Ic)

X = F or Cl .

Yet another method of synthesising chlorofluoromethylenetriphenylphosphorane, namely from Ph_3P, $CFCl_3$, and zinc (60 °C in DMF) [Eqn.(9)], also makes it possible to introduce into the Wittig reaction only aldehydes (heptanal and benzaldehyde) and an activated ketone (trifluoroacetophenone)[21,33]; the yield of the product from cyclopentanone is only 4%.[21]

Ketosugars were converted into chlorofluoromethylene derivatives on treatment with the ylid (Ic), generated from dichlorofluoromethylenephenylmercury in accordance with Eqn.(20).[15]

Chlorofluoromethylenetris(dimethylamino)phosphorane is apparently very convenient for the synthesis of α-chloro-α-fluoro-olefins by the Wittig reaction[18,32,33]. This ylid is generated by the dehalogenation of dichlorofluoromethyltris-(dimethylamino)phosphonium chloride on treatment with a tertiary phosphine [Ph_3P or $(Me_2N)_3P$—Eqn.(7)][18,32,33] or a metal [Eqn.(13)].[32,33]

The phosphorus ylid (Ih) is much more reactive than its triphenyl-substituted analogue (Ic), which makes it possible to carry out the Wittig reaction for non-activated ketones. At the same time the methods for the generation of this ylid ensure the formation of very stable "olefinating solutions" (see above). All this, together with the availability of the initial compounds, makes the use of chlorofluoromethylenetris(dimethylamino)phosphorane in the Wittig reaction particularly promising.

The reaction with aldehydes (heptanal and benzaldehyde) under mild conditions (60 °C, DMF) afforded chlorofluoro-olefins in quantitative yields[32].

The ylid (Ih), generated by the dehalogenation of the phosphonium salt by Ph_3P or Zn/Cu, successfully "olefinates" activated ketones[18,32,33]:

$$(Me_2N)_3P{=}CFCl + \underset{CF_3}{\overset{R}{\diagdown}}C{=}O \xrightarrow[\text{THF, triglyme, or PhCN}]{0\text{–}60^\circ} \underset{CF_3}{\overset{R}{\diagdown}}C{=}CFCl + (Me_2N)_3PO; \quad (75\text{—}100\%)$$

R = Ph or CF_3.

In dehalogenation by tris(dimethylamino)phosphine, fluoroketones cannot be introduced into the reaction, since they are cleaved[18,64]. However, this method (together with dehalogenation by a metal) is most convenient for reactions with non-activated ketones. The yield of the olefin from acetophenone is 56–70%;[18,32] the reaction does not take place with benzophenone and that with cyclopentanone gives an 18% yield of the olefin[32].

The reactions of the ylid (Ih) with the esters of fluoroacids, leading to alkyl fluoroalkenyl ethers, are of particular interest[18,32]¶:

$$\underset{(Ih)}{[(Me_2N)_3P{=}CFCl]} + \underset{RO}{\overset{R_F}{\diagdown}}C{=}O \xrightarrow[\text{or PhCN}]{\text{triglyme}} \underset{RO}{\overset{R_F}{\diagdown}}C{=}C\overset{F}{\underset{Cl}{\diagdown}} + (Me_2N)_3PO; \quad (21\text{—}90\%)$$

R_F=CF_3, HCF_2, $ClCF_2$, C_2F_5 or C_3H_7; R=Me, Et or iso-Pr.

The best results were obtained with methyl trifluoroacetate; methyl dichlorofluoroacetate and *N*,*N*-dimethyldifluoroacetamide do not enter into the reaction[32].

In contrast to the interaction with aldehyde and ketones, the reaction with esters is stereoselective—the Z-isomers are mainly formed[18,32].

The use of tributylchlorofluoromethylenephosphorane in the Wittig reaction is much less convenient than that of the ylids (Ic) and (Ih). The tributyl-substituted phosphorus ylid is more reactive in reactions with carbonyl compounds than the triphenyl-substituted ylid, but the instability of the ylid (If) precludes its wide-scale employment[14,16]. Nevertheless, when the ylid (If) was generated by the "halogenoacetate" method [Eqn.(17)], chlorofluoromethylenecyclopentane was obtained in 25% yield by the reaction with cyclopentanone (85 °C, triglyme, *in situ*); when the triphenylylid (Ic) is used under the same conditions, the yield of the olefin is only 9%.[14,16]

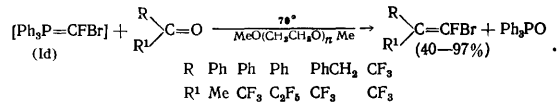
(d) *The introduction of the group =CFBr.* α-Bromo-α-fluoro-olefins are obtained by the Wittig reaction with the aid of bromofluoromethylenetriphenylphosphorane generated from triphenylphosphine and tribromofluoromethane [Eqn.(4)].[30]† The reaction can be carried out either *in situ* or

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¶These unsaturated ethers polymerise when an attempt is made to isolate them, but their formation has been rigorously demonstrated with the aid of NMR.[18,32]

†The use of the "halogenoacetate" method [Eqn.(16)] is less convenient[30].

with preliminary preparation of a stable "olefinating" solution. The ylid (Id) reacts fairly readily even with non-activated ketones. The Wittig reaction results in the formation of bromofluoro-olefins in the form of mixtures of *cis*- and *trans*-isomers (in proportions of ~1 : 1):



(Id) (40—97%)

R	Ph	Ph	Ph	$PhCH_2$	CF_3
R^1	Me	CF_3	C_2F_5	CF_3	CF_3

It is clear from the data presented that fluorine-containing halogenomethylenephosphoranes are highly reactive intermediates, which can be used successfully in the synthesis of fluoro-olefins and related compounds by the Wittig reaction. The use of a wide variety of methods for their generation and the introduction of different kinds of groups at the phosphorus atom permit a specific regulation of the stability and nucleophilic activity of these intermediates.

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Oxidative Dehydrodimerisation and Cyclisation Reactions of Unsaturated Hydrocarbons in the Presence of Oxide Catalysts

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The review is devoted to a comparatively new type of heterogeneous-catalytic processes—oxidative dehydrocoupling and cyclisation reactions of hydrocarbons with unsaturated bonds. The catalysts used in these processes and the rules governing their selection are examined. A systematic account is given of data on the kinetics and mechanisms of the reactions. Certain general characteristics of processes of this type are formulated and the problem of the selection of catalysts is discussed on their basis.
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I. INTRODUCTION

Oxidative dehydrodimerisation and cyclisation of unsaturated hydrocarbons constitute a comparatively new type of processes within the large class of heterogeneous catalytic reactions involving molecular oxygen. The first reports, demonstrating the possibility of these processes in principle, appeared in the patent literature in the middle 1960's and immediately attracted the attention of investigators.

The interest in the reactions under consideration is due to the possibility of processing numerous hydrocarbons with a mobile hydrogen atom in the α-position relative to the unsaturated bond. By specific catalytic synthesis, it is possible to obtain symmetrical dehydrodimers and in many instances the products of the subsequent reactions, which have practical applications. With the aid of these processes, it is possible to obtain, for example, diallyl and benzene from propene, *p*-xylene from isobutene, bibenzyl and *trans*-stilbene from toluene, and *p*-terphenyl from α-methylstyrene.

A number of advantages arise from the reactions being carried out in the presence of molecular oxygen compared with the familiar dehydrocyclodimerisation[1] and dehydrocyclisation[2] of paraffins and olefins. As a result of the oxidation of the eliminated hydrogen, these reactions are exothermic and the degree of conversion of the initial substance is not limited by the equilibrium conditions. The absence of carbon deposition ensures the stable operation of the catalyst and hence the continuity of the process. Finally, the oxidative version of the reaction is characterised by a narrower set of products, which greatly facilitates the isolation and purification of the required substances.

Apart from their applied importance, the oxidative dehydrodimerisation and cyclisation reactions of unsaturated hydrocarbons are of theoretical interest as an additional and convenient model for the application and refinement of the postulates of the theory of oxidative-reductive and acid–base catalysis.

Taken together, all these factors stimulated the publication during the last decade of a comparatively large number of patents and communications devoted to the above type of reactions. Among these, there have been reviews[3-5], which, however, suffer from being incomplete and one-sided. They describe mainly the compositions of catalysts found empirically and the conditions of the oxidative dehydrodimerisation and aromatisation reactions of the lower olefins. Considerably less attention has been devoted to the principles of the selection of catalysts and the problems of the reaction mechanisms, the principal data on which have been obtained very recently. Nor do they discuss the position occupied among other oxidative heterogeneous catalytic processes by dehydrocoupling reactions and the limits of the applicability to the latter of the special relations which have accumulated for total and partial oxidation reactions of hydrocarbons. The elimination of these gaps was one of the aims of the present review, which is based on studies published in the last 10–12 years.

II. OXIDATIVE DEHYDRODIMERISATION AND CYCLISATION OF OLEFINS

The principal products of the oxidative dehydrodimerisation and aromatisation of propene are hexa-1,5-diene and benzene and those obtained from isobutene are 2,5-dimethylhexa-1,5-diene and *p*-xylene. This difference from the thoroughly investigated reactions involving the partial oxidation of propene and isobutene to the corresponding unsaturated aldehydes and acids and oxidative dehydrogenation of *n*-butenes and isopentene to butadiene and isoprene is due to the differences between the compositions of the catalysts employed.

1. Process Catalysts

Table 1 presents the known catalysts of the oxidative dehydrodimerisation and cyclisation reactions of olefins. The vast majority of them consist of metal oxides. The use of noble metals, for example silver[6,7] and palladium[8], for this purpose has not developed owing to their high cost and the lack of significant advantages over oxide catalysts. For a number of technological reasons, it is difficult to carry out the process in the presence of melts of metals such as bismuth and tin[9] or salt melts of the type of lithium iodide[10].

The simple metal oxides are as a rule relatively ineffective as regards the formation of diolefinic and aromatic hydrocarbons. Among the last number of specimens investigated

Table 1. Catalysts for the oxidative dehydrodimerisation and aromatisation of olefins.

Catalyst	Method of preparation of catalyst	Reaction conditions*	Conversion of olefin, %	Selectivity, %		Refs.
				w.r.t. diolefin**	w.r.t. aromatic products	
Metallic Ag with added alkaline earth metal oxides	decomposition in a stream of air at 220 °C of silver carbonate deposited from aqueous suspension	500°; $C_3H_6 : O_2 = 39 : 1$; $t_c = 0.56$ s	1.1	61.9	—	6,7
Metallic Bi, Sn, and their alloys in the liquid state	–	593°; C_3H_6 : air = 1 : 2; t_c = 0.2—3 s	16.6	22.4	54.4	9
Fused 98% LiI + 2LiOH mixture	–	480°; iso-$C_4H_8 : O_2 = 4.2 : 10$; t_c = 0.1—5 s	36.5	—	68.8	10
Bismuth oxide	decomposition of the hydroxide at 550 °C in 24 h	575°; C_3H_6 : air : He = 2 : 5 : 10, t_c = 2.1 s	28.5	57.0	5.4	12, 13
Indium oxide	decomposition of the hydroxide at 560°	480°; $C_3H_6 : O_2 = 5 : 1$ t_c = 1.2 s	—	22.6	40	14
Thallium oxide	decomposition at 500° of the hydroxide deposited from nitrate solution by sodium hydroxide	520°; $C_3H_6 : O_2 = 10 : 1$ t_c = 4 s	—	78.0	—	14
Lead oxide deposited on Al_2O_3	repeated impregnation of the carrier *in vacuo* with a solution of the nitrate salt; heat treatment at 700°	493°; $C_3H_6 : O_2 = 15.7 : 1$; pressure —3.2 atm; t_c = 0.04 s	5.6	76	—	15, 16
Bismuth–tin oxide catalyst; Bi : Sn = (1–9) : (9–1) (best 1 : 1)	heat treatment of a mixture of individual oxides at 540° for 16 h	470°; $C_3H_6 : O_2 = 1.4 : 1$; t_c = 3 s	24.5	—	61.5	19, 20
Bismuth–tin oxide catalyst (Bi : Sn = 2 : 3)	heat treatment of a mixture of bismuth nitrate and tin dioxide at 750° for 28 h	575°; C_3H_6 : air : He = 2 : 5 : 10, t_c = 1.1 s	18	24.2	27.5	22
Bismuth–phosphorus oxide catalyst (Bi : P = 2 : 1)	deposition from an acidified solution of bismuth nitrate and ammonium phosphates, drying, and heat treatment at 500°	500°; $C_3H_6 : O_2 = 1 : 1.6$; t_c = 1.0 g s ml^{-1}	85.8	—	44.9	25
Bismuth–phosphorus oxide catalyst (Bi : P = 2 : 1 with addition of 0.6% Na_2O)	joint deposition at pH 6; heat treatment of dried deposit at 600°	550°; $C_3H_6 : O_2 = 5.6 : 1$; t_c = 0.36 s	6.9	47	—	28
Bismuth–titanium oxide catalyst (Bi : Ti = 1 : 1)	heat treatment of a mixture of oxides	550°; $C_3H_6 : O_2 : N_2 = 1 : 2 : 8.1$; t_c = 2.0 s ml^{-1}	81.9	—	29.1	11, 30
Bismuth–titanium oxide catalyst (Bi : Ti = 4 : 3)	heat treatment of a mixture of bismuth nitrate and titanium oxide at 750°	575°; C_3H_6 : air : He = 2 : 5 : 10; t_c = 1.2 s	20.2	26.8	24.6	22
Bismuth–titanium oxide catalyst (Bi : Ti = 2 : 1)	evaporation of a solution of bismuth nitrate and titanium dioxide in dilute nitric acid, drying, and heat treatment at 500°	575°; C_3H_6 : air : He = 2 : 5 : 10; t_c = 2.1	22.0	38.4	17.5	13
Bismuth–zinc oxide catalyst [Bi : Zn = (1–3) : (3–1)]	heat treatment of a mixture of bismuth nitrate and zinc acetate at 600° for 4 h	585°; $C_3H_6 : O_2 = 5.6 : 1$; t_c = 0.36 s	3.3	58.5	—	23
Mixture of bismuth and indium oxides on a carrier (Bi : In = 7 : 3)	–	500°; iso-$C_4H_8 : O_2 = 1 : (0.3—1)$; t_c = = 1—15 s	26.2	10.5	50.3	33
Bismuth–antimony oxide catalyst (Bi : Sb = 1 : 1)	heat treatment of a mixture of oxides in air at 600° for 4 h	585°; $C_3H_8 : O_2 = 5.6 : 1$; t_c = 36 s	10.0	50.0	—	23
Bismuth and antimony oxides on a carrier promoted with Na, Cu, or Zr oxides	–	420°; iso-$C_4H_8 : O_2 = 4 : 1$; t_c = = 0.45 s	32.0	65.0	—	34
Bismuth–nickel oxide catalyst (Bi : Ni = 1 : 1)	mixing and heat treatment of individual oxides at 540°	470°; C_3H_6 : air . $H_2O = 1 : 4 : 3$; t_c = 7.5 s	51.2	25.3	46,5	35
Bismuth–copper oxide catalyst (Bi : Cu = 1 : 1)	heat treatment of a moistened mixture of oxides at 540°	470°; iso-C_4H_8 . air : $H_2O = 1 : 4 : 3$; t_c = 7.5 s	51.5	30.5	45,6	35
Bismuth–iron oxide catalyst (Bi : Fe = 1 : 1)	decomposition of a mixture of bismuth and iron nitrates	575°; C_3H_6 : air : He = 2 : 5 : 10; t_c = 1.1 s	16.1	20.7	14.6	22
Bismuth–iron oxide catalyst (Bi : Fe = 2 : 1)	heat treatment of a mixture of oxides at 600–700° for 4 h	586°; $C_3H_8 : O_2$ = 5; 7 : 1; t_c = 0.36 s	6.8	49.0	9.8	36
Bismuth–cadmium oxide catalyst (Bi : Cd = 5 : 3.5 with added lead and magnesium oxides)	heat treatment of a moistened and dried mixture of oxides at 540° for 16 h	500°; C_3H_8 (iso-C_4H_8) : air : H_2O = = 1 : 8 : 2; t_c = 4.3 s	20.0 (17.0)	—	55.2 (56.3)	37
Bismuth oxide deposited on alundum with added 2.8% K_2O	successive impregnation of the carrier with solutions of bismuth nitrate and potassium hydroxide, drying at 120°, and heat treatment at 550°	550°; $C_3H_6 : O_2 : N_2 = 10.8 : 1 : 71.5$	12.0	77.0	—	44
Bismuth–zirconium oxide catalyst (Bi : Zr = 2 : 3)	decomposition of a mixture of bismuth nitrate and zirconium oxide	575°; C_3H_6 : air : He = 2 : 5 : 10; t_c = 1.1 s	18.0	28.0	14.8	22
Bismuth–niobium catalyst (Bi : Nb = 1 : 1)	heat treatment of a mixture of bismuth nitrate and niobium oxide	575°; C_3H_6 : air : He = 2 : 5 : 10; t_c = 2.1 s	2.6	28.2	27.8	13
Bismuth–tungsten oxide catalyst (Bi : W = 2 : 1)	heat treatment of a mixture of bismuth nitrate and tungsten trioxide	575°; C_3H_6 : air : He = 2 : 5 : 10; t_c = 2.1 s	14.4	6.1	19.9	13
Bismuth arsenate $BiAsO_4$ (monazite)	evaporation of a mixture of solutions of bismuth nitrate and the ammonium salt of a hydroxy acid with subsequent heat treatment	500°; $C_3H_6 : O_2 : N_2 = 1 : 2 : 8.1$; t_c = = 2 g s ml^{-1}	69	—	33.8	11, 30
Bismuthyl sulphate $(BiO)_2SO_4$	decomposition of bismuth sulphate in air at 600°	500°; $C_3H_6 : O_2 : N_2 = 1 : 2 : 8.1$; t_c = = 2 g s ml^{-1}	61	—	10.1	11, 30
Manganese and sodium oxides (Mn : Na = 1 : 2) on Al_2O_3, SiC, and aluminosilicate carriers	fusion of manganese dioxide with Group IA and IIA metal oxides or decomposition of a mixture of acetates, oxalates, and formates	638°; $C_3H_6 : O_2 = 1 : 1$; t_c = 0.05 s	—	54.5	—	47, 48
Mixture of manganese and sodium oxides (Mn : Na = 1 : 2.3) on alumina	impregnation of the carrier with solutions of manganese and sodium acetates	627°; $C_3H_6 : O_2 = 4 : 1$; t_c = 0.1—5 s; HBr introduced into gas phase	9.0	7.4	46.6	49
Tin–cadmium oxide catalyst (Sn : Cd = 0.33 : 1)	evaporation of a mixture of cadmium oxide and a solution of metallic tin in nitric acid followed by heat treatment of the deposits at 400° for 6 h	570; iso-$C_4H_8 : O_2 = 1 : 2$; t_c = 3 s	62.5	13.4	65.5	50

Table 1 (cont'd.).

Catalyst	Method of preparation of catalyst	Reaction conditions*	Conversion of olefin, %	Selectivity, %		Refs.
				w.r.t. diolefin**	w.r.t. aromatic products	
Palladium–dimethyl sulphoxide complex deposited on rock	impregnation of the carrier with a solution of $K[Pd(DMSO)Cl_2]$ in DMSO and with an acid aqueous solution of $PdCl_2$	500°; $C_3H_6 : O_2 = 1 : 1$	58.2	75.6	11.0	51, 52

*t_c = reaction time.

**The diolefin should be understood as hexa-1,5-diene in the oxidation of propene and 2,5-dimethylhexa-1,5-diene in the oxidation of isobutene.

***The main aromatic products of the conversion of propene and isobutene are benzene and *p*-xylene respectively.

by Seiyama[11], bismuth, cadmium, zinc, and tin oxides proved to be comparatively selective in the oxidative dehydroaromatisation of propene. Analogous data have been published for bismuth oxide[12,13]. The selectivity with respect to the desired products reaches 60% in the presence of the above catalysts for a degree of conversion of the initial olefins of 28%. Indium and thallium oxides are also relatively selective[14] in the presence of a large excess of the olefin in the initial mixture. In the presence of these catalysts the overall selectivity with respect to diallyl and benzene is 60–80% for a conversion of propene less than 1%. Lead oxide has similar parameters[15–17].

Almost all the individual oxides mentioned above exhibit a low activity but a comparatively high selectivity. An additional characteristic feature of lead and thallium oxides is instability of activity due to the reduction of lead oxide to the inactive metal[17] and the volatility of thallium (I) compounds formed in the catalytic process[18]. Two-component oxide systems are more active in oxidative dehydrodimerisation and aromatisation reactions of the lower olefins. The largest group consists of catalysts based on bismuth oxide. Combinations of the latter with the oxides of tin[19–24], phosphorus[25–29], titanium[13,22,30,31], zinc[23,32], indium[33], antimony[23,24], nickel[35], copper[34,35], iron[22,35,36], cadmium[30,37], lead[37], manganese[38], and a number of other metals are effective.

The increased activity of complex oxides compared with simple oxides is apparently associated with the formation of definite catalytically active compounds. In the study of the phase compositions of bismuth–tin[39–41], bismuth–iron[36], and bismuth–titanium[42] oxide catalysts, the existence in the latter of bismuth pyrostannate ($Bi_2Sn_2O_7$), orthoferrite ($BiFeO_3$), and pyrotitanate ($Bi_2Ti_2O_7$) respectively was observed. The catalysts exhibit the maximum activity for approximately the above ratios of the elements. The data of the present author and his coworkers[41], illustrated in Fig. 1, show that the rate and selectivity of the formation of the products of the oxidative dehydrodimerisation and aromatisation of propene in the presence of bismuth–tin oxide catalysts vary in parallel with their content of the $Bi_2Sn_2O_7$ phase. A similar variation has also been established for specimens with an identical ratio of bismuth and tin obtained by different methods and differing in phase composition as a result[43].

When other metal oxides are introduced into bismuth oxide, a change in the composition of the reaction products is sometimes observed together with an increase of the overall activity. Thus, when zinc oxide[32], tin dioxide[40], and indium oxide[33] are used as the second component, the fraction of aromatic hydrocarbons increases significantly compared with pure bismuth oxide, in the presence of which the main reaction product is a diolefinic hydrocarbon.

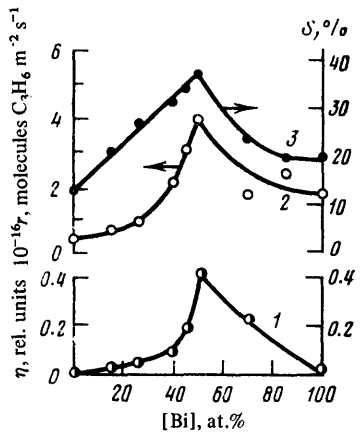


Figure 1. The influence of the composition of bismuth–tin oxide catalysts on the relative content η of the $Bi_2Sn_2O_7$ phase (curve *1*), the rate *r* (curve *2*), and the selectivity *S* (curve *3*) in the overall formation of diallyl and benzene[41].

Small amounts of added alkali metal oxides cause an appreciable increase of the selectivity of bismuth-containing catalysts in olefin dehydrodimerisation and aromatisation reactions[24,28,34,44,45]. Thus, according to a patent[44], the introduction of 2.8% of potassium oxide into deposited bismuth oxide increases the selectivity with respect to hexa-1,5-diene from 70 to 77% for the same degree of conversion of propene. Small amounts of alkali metal oxides have a similar influence on the catalytic properties of tin dioxide[11,30]. Fig. 2 shows that the maximum selectivity in the formation of benzene is observed in the presence of 5 at.% of sodium oxide in tin dioxide. These amounts of sodium oxide are uniformly dispersed on the surface of tin dioxide and do not form a chemical compound with the latter[5]. In the presence of more than 5 at.% of sodium dioxide, the uniformity of the distribution breaks down and the compound Na_2SnO_3, completely inactive in the oxidative reaction of propene, is

formed[5]. For this reason sodium bismuthate, while fairly selective, is apparently characterised by a low activity compared with bismuth oxide[46].

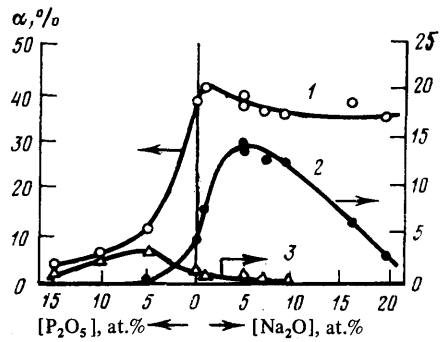


Figure 2. The promoting influence of sodium and phosphorus oxides on the catalytic properties of tin dioxide: *1*), *2*), and *3*) degrees of conversion of propene into carbon dioxide, benzene, and acrolein respectively[11].

In conclusion of the brief consideration of bismuth-containing catalysts, one must note that the introduction of zirconium[22], niobium[13], tungsten[13], arsenic[11,30], sulphur[11], and aluminium[30] compounds into bismuth oxide does not improve significantly and in some cases actually impairs its catalytic properties.

Among other oxide systems, mention should be made of the sodium–manganese oxide system[47–49]. While exhibiting a satisfactory selectivity with respect to the oxidative dehydrodimerisation and aromatisation products (50–55%), these catalysts have a low activity even at high temperatures: at 627 °C the degree of conversion of propene in their presence does not exceed 5–10%. The tin–cadmium oxide system is more active[50]. Thus, in the presence of the oxide catalyst with the composition Sn/Cd = 0.4, the degree of conversion of isobutene reaches 65–67% for a selectivity in the formation of *p*-xylene of 58–65%.

Attempts have been made to use "heterogenised" metal complex catalysts in the oxidative dehydrodimerisation of propene[51,52]. It was shown that, in the presence of palladium- and iron-containing complexes deposited on a natural silicate mineral, diallyl and benzene are formed at lower temperatures (200–300 °C) and in larger amounts than in the presence of bismuth oxide. However, here it is necessary to solve the problem associated with the stability of the activity of catalysts of this kind.

It has been suggested in a number of patents[53–56] that the reactions be carried out in the absence of gaseous oxygen and that the hydrogen split off in the dehydrodimerisation and aromatisation of the olefin be combined with the oxygen of the oxide, i.e. that the catalyst be used as an oxidant. It appears difficult to assign this version of the process to oxidative heterogeneous-catalytic reactions and to specify a clear-cut boundary between them and dehydrocyclodimerisation processes[1]. This review therefore deals only with processes carried out in the presence of molecular oxygen.

Thus the foregoing permits the conclusion that the catalysts of oxidative dehydrodimerisation and aromatisation reactions of olefins differ appreciably in their qualitative composition from the known partial oxidation catalysts containing as a rule molybdenum, tungsten, vanadium, antimony, arsenic, and tellurium oxide compounds. From this standpoint, the report[57] that the uranium–antimony catalyst, which is extremely effective in the partial oxidation and oxidative dehydrogenation reactions of olefins, is active in the dehydrodimerisation reaction appears unexpected[58,59].

2. Certain Characteristics of the Selection of Catalysts

The catalytic activities of a large number of simple and complex oxides with respect to the total oxidation of hydrocarbons are known[60–62] to be determined by the binding energy of the surface oxygen—the smaller the bond strength, the higher the rate of oxidation. The situation is more complex in partial oxidation processes whose most important characteristic is selectivity with respect to a specific substance. It has been shown for a number of reactions[60,63,64] that the selectivity with respect to mild oxidation products increases with increasing energy of the oxygen–catalyst bond.

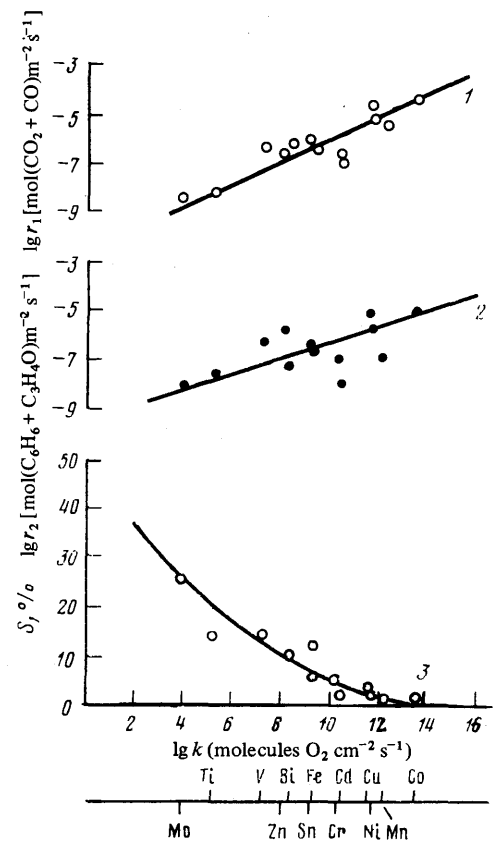


Figure 3. Dependence of the rate of total oxidation r_1 (curve *1*) and the rate r_2 (curve *2*) and selectivity S (curve *3*) in the allyl oxidation of propene[11] in the presence of simple oxides on the mobility of the surface oxygen, i.e. on the rate constant for the homomolecular exchange of oxygen k.[102]

An attempt to test the possibility of the existence of correlations of this kind for the oxidehydroaromatisation of propene was undertaken by Seiyama[11], who used the heats of formation of the individual oxides as a measure of the strength of binding of oxygen in them. When these quantities were compared with the rates of extensive and mild (acrolein + benzene) oxidative conversion of propene, it was found that the oxides can be divided into two groups, differing, according to the author, by the type of oxygen isotope exchange occurring in them. This factor as well as the considerable scatter of the points are apparently caused by the fact that the heats of formation of the oxides characterised their bulk-phase and not surface properties. It is more correct to use for this purpose the heats of desorption of the equilibrium oxygen[65] or the rates of homomolecular oxygen isotope exchange[66]. Fig. 3 shows that in the latter case the subdivision of oxides into two groups disappears and the correlation is more clear-cut.

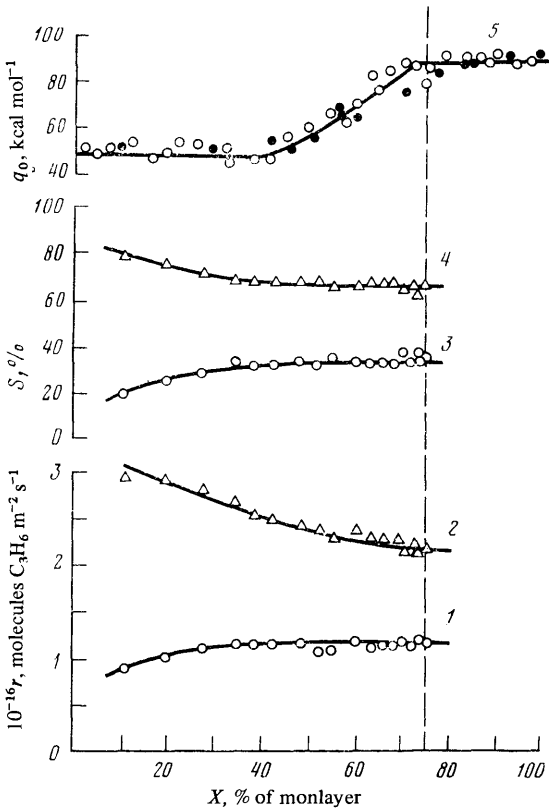


Figure 4. The influence of the degree of reduction X of the surface of the bismuth–tin oxide catalyst on the rate r and the selectivity S in the formation of diallyl (curves 1 and 3) and carbon dioxide (curves 2 and 4) and on the binding energy of oxygen q_0 (curve 5). The stationary state of the catalyst is indicated by a dashed line[69].

Fig. 3 also shows that the catalytic activity with respect to partial oxidation increases with increase of the mobility of surface oxygen to a smaller extent than in the case of total oxidation. As a result, the selectivity with respect to the overall formation of acrolein and benzene falls with decrease of the strength of binding of oxygen to the catalyst. It may be that this behaviour is caused by the fact that in the rate-limiting stage of the total oxidation reaction a larger number of oxygen–catalyst bonds are broken than in dehydroaromatisation, which is similar to the explanation used for the extensive and mild oxidation reactions of hydrocarbons[67,68].

A test of the validity of the above correlations for complex oxide catalysts of the oxidehydrodimerisation of olefins is at present difficult owing to the lack of data for the binding energies of surface oxygen in such catalysts. The possibility of the existence of correlations of this kind is supported by the results of a comparison of the relations presented in Fig. 4 between the catalytic activities and the binding energies of oxygen, on the one hand, and the degree of reduction of the bismuth–tin oxide catalyst, on the other[69]. Evidently the removal of weakly bound oxygen from the surface during the catalytic process reduces the selectivity of the total oxidation reaction and increases that with respect to diallyl - the product of the mild conversion of propene.

The problem of the way in which the strength of binding of oxygen to the catalyst influences the rate of partial oxidation of olefins to unsaturated aldehydes, on the one hand, and the rate of dehydrodimerisation, on the other, is also important. However, the relation between these quantities has not so far been discovered. One cannot rule out the possibility that different forms of surface oxygen participate in the reaction.

The dependence of the mode of oxidative transformation of olefins on the acid—base properties of the catalyst has been studied in greater detail. For many simple[11] and bismuth-,[30] zinc-,[70] cadmium-,[70] and tin-containing[71] binary oxides, it has been established that an increase of the acidity of the catalyst entails a decrease of the rate and selectivity of the formation of propene dehydrodimerisation and aromatisation products and of the increase of the yields of acrolein. The electronegativity of the metal cations[11,70], the strengths of the acid centres found by titration with *n*-butylamine[30,72], and the activity in the isomerisation involving the double bond in but-1-ene[71] are used as characteristics of the acid properties. Table 2 presents as an example, data[30] whereby one can follow the above relation between the selectivity in the oxidehydroaromatisation and partial oxidation reactions of propene and the acidity determined with the aid of Hammett indicators for bismuth-containing oxide catalysts.

Table 2. Selectivity in the allyl oxidation reactions of propene and the acid strength of bismuth-containing catalysts {500°; $[C_3H_6] = 9$ vol.%; $[O_2] = 18$ vol.%; conventional contact time 1.0 g s ml^{-1}}.[30]

Catalyst	Selectivity, %		Acid strength H_0
	benzene	acrolein	
$2Bi_2O_3 \cdot P_2O_5$	49.0	0	+7.1—+6.8
$BiAsO_4$	33.8	5.8	+6.8—+4.0
$BiPO_4$ (high-temperature form)	26.9	6.6	+6.8—+4.0
$Bi_2O_3 \cdot 2TiO_2$	18.0	0.3	+7.1—+6.8
$(BiO)_2SO_4$	10.1	4.0	+6.8—+4.0
$BiPO_4$ (monazite form)	9.1	38.6	+1.5—−3.0
$(BiO)_2MoO_4$	0	66.1	+3.3—+1.5
$Bi(BiO)(MoO_4)_2$	0	91.7	+1.5—−3.0
$Bi_2(MoO_4)_3$	0	94.9	+1.5—−3.0

This general relation makes it possible to regulate the acid–base and hence catalytic properties of the catalyst by promoting it with oxides of different kinds; this is clearly illustrated in Fig. 2. The introduction of an alkali metal oxide into tin dioxide in amounts ensuring the homogeneity of the system increases the selectivity of the oxidehydrocyclisation of propene, while the addition of an oxide having acid properties (P_2O_5) suppresses this reaction and stimulates the partial oxidation of the olefin to an aldehyde.

In explaining the correlation between selectivity and acidity, it has been suggested that[5,30] the oxidehydrodimerisation of propene proceeds, like oxidation to acrolein, via an intermediate allyl compound, which either carries a weak positive charge or is neutral. As a result of the localisation on an "acid" adsorption site, regarded as a Lewis acid, of the electron of the allyl radical, the latter becomes similar to a cation and sensitive to the addition of an oxygen anion. At sites with a lower acid strength the intermediate compounds are of a more "radical type", which favours their dimerisation. Within the framework of this hypothesis, the promoting effect of basic and acid oxides on the catalytic properties of tin dioxide discussed above can be accounted for by a change in the electronic state of the centre for the adsorption of olefin (Sn^{4+}) via the $Sn^{4+}–O^{2-}–M^{n+}$ linkage in accordance with the electronegativity equalisation principle[11].

Simultaneously with the change in the electronic state of the allyl fragment, the strength of the bond between the allyl fragment and the catalyst surface can apparently also vary as a function of the electronegativity of the adsorption centre[70–72]. On specimens with a reduced acidity, a lower bond strength and an increased mobility of allyl radicals is expected, which increases the probability of their recombination. Conversely, when allyl compounds are bound strongly to the surface there is a greater number of chances of conversion into acrolein or total oxidation products.

It is suggested that the activity of the catalyst in the test reaction involving the migration of the double bond in but-1-ene can be used as a measure of the relative strength of the olefin–catalyst bond[73]. This can be done if the isomerisation is carried out with participation of aprotic centres (the ratio of the *cis*- and *trans*-isomers of but-2-ene formed should be two[74]) under conditions close to those in oxidative catalysis[75]. While maintaining these conditions, it proved possible[71] to show that, with intensification of the isomerising capacity of the catalyst and hence with the strengthening of the bond between the adsorbed olefin and the catalyst, the rate of dehydrodimerisation of propene falls and that of its partial oxidation increases; the results of this study are presented in Fig. 5.

For an unambiguous test of the above relations, it is necessary to compare the selectivity not with the overall acidity, as was done in the studies mentioned above, but with acidity of a definite type, in particular with the strength and concentration of the acid Lewis centres. However, the methods for the determination of the acidity of the surface oxides available at present[76] preclude a reliable solution of this problem. Furthermore, the acidity parameters determined by the traditional titration and base adsorption methods correspond to conditions very remote from those in catalytic reactions.

Thus the features described show that catalysts of the oxidative dehydrodimerisation of olefins must have weakly basic properties ensuring a moderate strength of the binding of allyl complexes to the centre of the catalyst and their adequate mobility. Furthermore, the catalysts should not contain components causing the oxidation of the above complexes to unsaturated aldehydes. It has been shown[77] that highly charged ions of electronegative elements such as molybdenum, tungsten, vanadium, tellurium, antimony, etc. play the role of such components.

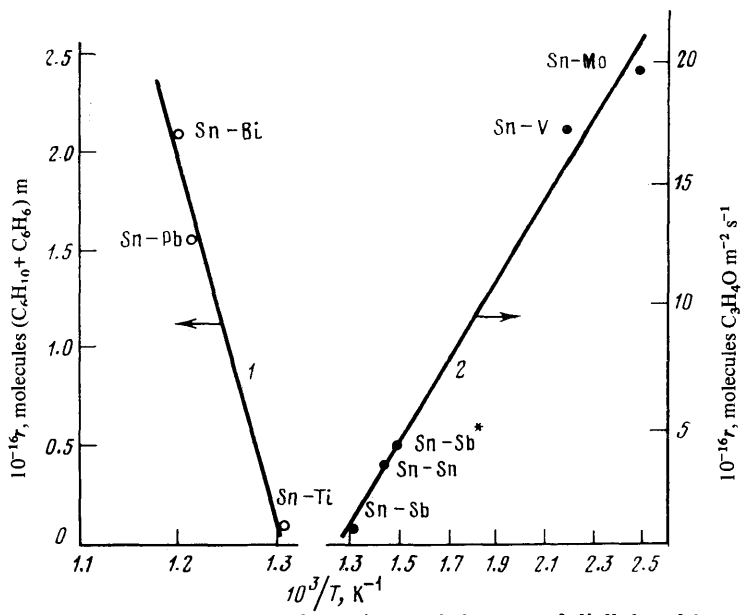


Figure 5. Dependence of the rates of formation r of the sum of diallyl and benzene (line *1*) and acrolein (line *2*) on the isomerising capacity of tin-containing oxide catalysts (on the reciprocal of the temperature $1/T$ corresponding to the attainment of the specified rate of isomerisation of but-1-ene)[71].

These two requirements are satisfied by the oxides of non-transition elements located in the lower left-hand section of the Periodic System. These include zinc, gallium, cadmium, indium, tin, thallium, lead, bismuth, etc. (zinc and cadmium are usually regarded as non-transition elements, because they do not in fact exhibit a variable valence and do not form compounds in which the *d* shell is unfilled[78]). The oxides of all these elements exhibit weakly basic or amphoteric properties and are active to different extents in the oxidative dehydrodimerisation and aromatisation reactions of lower olefins. A considerable proportion of them is also characterised, according to Sokolovskii and Bulgakov[79], by nearly optimum nucleophilic properties of oxygen required to abstract the proton from the olefin and form an allyl complex. The boundary of elements potentially active in the above processes runs along the diagonal drawn through aluminium, germanium, antimony, and polonium. The main product of the oxidative transformation of propene on pure antimony tetroxide[80] and certain antimony-containing oxide catalysts[57,81] is acrolein, while diallyl and benzene are formed in smaller amounts.

Alkali and alkaline earth metal oxides exert a positive influence on the selectivity of the processes when they are introduced in small amounts into the catalyst.

A considerable proportion of the oxides of the elements enumerated above are also incorporated in the set of catalysts recommended by Trimm[82,83]. The author assumes that diallyl is formed by the dimerisation of two allyl radicals linked to the same metal ion whose characteristic valence states differ by two charge units.

3. Kinetics and Mechanisms of the Reactions

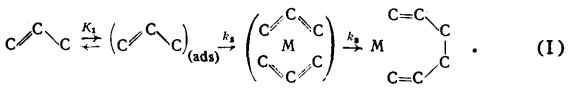
A relatively small number of studies devoted to the kinetics and certain problems of the mechanism of the oxidation of lower olefins to diolefinic and aromatic hydrocarbons are described in the literature. Kinetic studies have been made on the oxydehydrodimerisation of propene on individual thallium[18] and indium[84] oxides. For low degrees of conversion of the hydrocarbon, the main products are hexa-1,5-diene and carbon dioxide, while in the presence of indium oxide acrolein is also formed. Under these conditions, the rates of formation of diallyl and CO_2 are proportional to the concentrations of propene and oxygen raised to a power of 0.4–0.5 and the reactions are inhibited by diallyl and acrolein.

The author described the kinetic data[18,84] by the Langmuir–Hinshelwood equation. According to the model which they adopted, the rate-limiting stage in the process is the formation of hexadiene by the interaction of two molecules of propene and the dissociated oxygen, all adsorbed on the surface. Propene, diallyl, and acrolein are adsorbed competitively at the same sites, while oxygen is adsorbed at other sites. The catalytic centres are tervalent thallium or indium ions, capable of forming π-complexes with the olefin.

In the oxidation of isobutene to 2,5-dimethylhexa-1,5-diene on the same indium oxide, it was shown that the reaction is of first order with respect to the olefin and has a fractional order (0.8) with respect to oxygen[85,86]. This result, as well as the weak adsorption of isobutene on the catalyst, forced the authors to postulate that in the case of isobutene two gas-phase molecules of the latter interact with the dissociatively adsorbed oxygen. In other respects the reaction mechanism does not differ from that adopted for reaction with propene.

The individual kinetic parameters of the reactions under consideration have been determined for a number of bismuth-containing catalysts. Thus, on simple bismuth oxide, the state of dehydrodimerisation of propene is directly proportional to the partial pressure of the hydrocarbon and is independent of the oxygen concentration[12]. It has also been shown that the reactions on the bismuth–iron[87] and bismuth–tin[39] oxide catalysts are of first order with respect to the propene. For the latter catalyst, the reaction was found to be of first order also with respect to oxygen.

The kinetics of the process in the presence of the bismuth–tin catalyst were investigated in greater detail by Seiyama et al.[88], who studied the oxidative dehydrodimerisation of C_3–C_4 olefins under conditions where the products are dehydrodimers and carbon dioxide formed simultaneously. It was found that the rate of dimerisation is proportional to the partial pressure of the hydrocarbon raised to a power of 1.5–2.0 and is independent of the oxygen content in the mixture. The order of the extensive oxidation reaction was found to be close to unity with respect to the olefin and to have a fractional value (~0.5) with respect to oxygen. The authors interpreted[88] the results of the kinetic measurements within the framework of the Langmuir–Hinshelwood scheme for an ideal adsorbed layer, as in the study of Trimm and Doerr[84]. It was assumed that the adsorption of the olefin involves the formation of a π-complex which interacts weakly with the hydrogen atom in the α-position relative to the unsaturated bond and in the vicinity of an oxygen atom on the catalyst surface. Next, the above hydrogen atom is abstracted and a complex of the metal ion with two allyl radicals is formed via the mechanism



(I)

Since the reaction order is nearly two with respect to the olefin and the reaction rate constant varies in opposition to the dissociation energy of the olefin C–H bond in the allyl position (Fig.6), the authors had to assume that the rate-limiting stage is surface dimerisation (k_2). The equation

$$r_{C_6H_{10}} = k_2\left(\frac{K_1 p_{C_3H_6}}{1 + K_1 p_{C_3H_6}}\right)^2 \qquad (1)$$

which follows from this mechanism describes satisfactorily the experimental data obtained on two specimens of the bismuth–tin catalyst. The activation energy for the process on a highly selective specimen is lower by 20 kcal mol^{-1} than on a specimen with a low selectivity, which has been attributed to the presence on the surface of the former of more active centres for the allyl–hydrogen cleavage of propene[5].

Appreciably different kinetic characteristics of the oxidative dehydrodimerisation of propene have been obtained recently in the presence of a bismuth–tin oxide catalyst[89]. These are in the first place a negative variation of the rate of formation of diallyl with the partial pressure of oxygen in the reaction mixture, illustrated in Fig.7*b*, and in the second place the observation that an increase of temperature entails an appreciable decrease of the reaction order with respect to the olefin (from 2.0 at 450 °C to 1.2 at 530 °C). It may be that the discrepancies with the data of Seiyama et al.[88] are caused by the significant differences between the methods of preparation of the specimens, which frequently determine the phase composition and surface properties of the catalyst.

The observed relations can be accounted for by the following scheme[89]

$$\begin{aligned} Z + O_2 &\xrightarrow{k_1} ZO_2 \,, \\ Z + ZO_2 &\underset{}{\overset{K_2}{\rightleftarrows}} 2ZO \,, \\ ZO + C_3H_6 &\xrightarrow{k_3} C_3H_5ZOH \,, \\ C_3H_5ZOH + C_3H_6 &\xrightarrow{k_4} C_6H_{10} + H_2O + Z \end{aligned} \qquad (II)$$

(here Z denotes a reduced site on the catalyst surface). Under the conditions investigated, the following kinetic equation of the fractional-rational type corresponds to this scheme:

$$r_{C_6H_{10}} = \frac{k'k''p^2_{C_3H_6}}{k'p_{C_3H_6} + k'p_{O_2}}, \qquad (2)$$

where $k' = K_2k_3^2/2k_1$ and $k'' = k_3k_4/(k_3 + k_4)$. Eqn.(2) describes the experimental data satisfactorily (Fig.7). Other forms of kinetic equations, particularly those of the Langmuir–Hinshelwood type, give a poorer agreement with experiment[90].

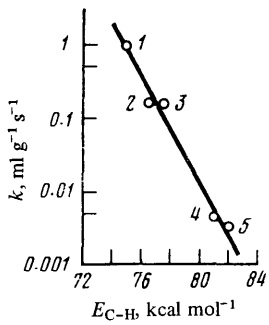


Figure 6. Dependence of the rate constant for the oxide-hydrodimerisation of olefins k on the dissociation energy E of the C–H bond in the methyl group: *1*) but-1-ene; *2*) *cis*-but-2-ene; *3*) *trans*-but-2-ene; *4*) isobutene; *5*) propene[88].

Scheme (II) presupposes that diallyl is formed by the interaction of a gas-phase propene molecule with a surface compound of the allyl type. This mechanism, which may be referred to as of the "impact" type, does not rule out the possibility of the operation of mechanism (I), which involves the stage of the surface dimerisation of allyl radicals. Furthermore, the two mechanisms can coexist. The contribution of mechanism (I) to the overall rate of the process will be evidently determined by the mobility of the allyl compound on the surface, which can depend on the reaction conditions and on the nature of the catalyst. In particular, the acid–base properties of the catalyst can play a significant role in this process[30,71].

In the interpretation of kinetic data in terms of the above mechanism, it is assumed that the oxidative dehydrodimerisation of the olefin proceeds via the formation of a π-allyl complex. This hypothesis is based on the following facts. In the presence of certain oxide catalysts[25,84], the oxide-hydrodimerisation of propene is accompanied by the formation of acrolein, which is known to proceed via an intermediate allyl compound[91]. On the bismuth–tin oxide catalyst, allyl chloride and bromide are converted into benzene in the presence of oxygen, while 2-bromopropene undergoes total oxidation[92]. Finally, the composition and structure of the diolefinic and aromatic hydrocarbons formed are not inconsistent with the allyl mechanism[93].

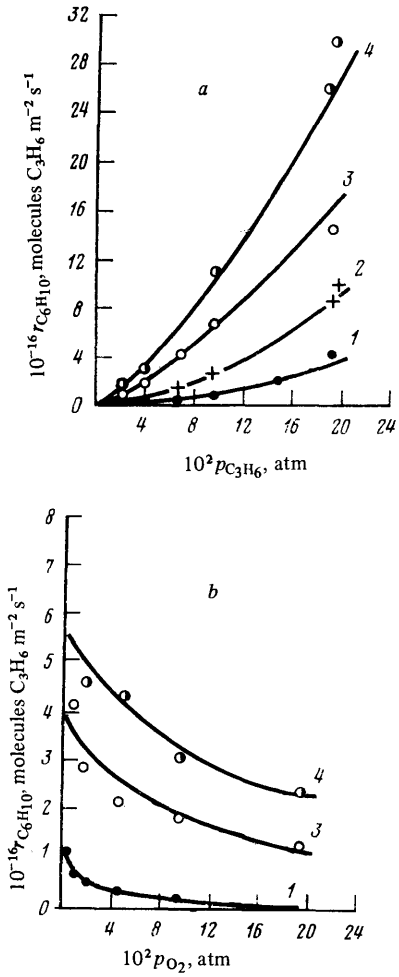


Figure 7. Dependence of the rate of formation of diallyl r on the partial pressures p of propene (*a*) and oxygen (*b*) at different temperatures (°C): *1*) 450; *2*) 485; *3*) 500; *4*) 530. The continuous curves were calculated by Eqn.(2) and the circles represent experimental data[89].

Attempts to demonstrate directly the existence of π-allyl complexes on the surface of the oxidative dehydroaromatisation catalysts have been made. Two forms of propene adsorbed on zinc oxide have been found[94–96] by infrared spectroscopy. At room temperature mainly a π-complex is formed, which is converted at higher temperatures (70 to 125 °C) into a π-allyl surface compound. The ability of zinc oxide to form allyl surface compounds of the radical-like type in the adsorption of propene has been confirmed by EPR[97].

The presence of allyl radicals has been detected also in the gas phase over manganese oxide[47,98,99] and zinc oxide[99] catalysts. It has been established by mass spectrometry that the radical concentration increases with temperature. On the other hand, the latter does not affect the significantly smaller content of free radicals over bismuth molybdate, which is a typical catalyst of the partial oxidation of olefins. These results have been explained[99] in terms of the ideas, described above, concerning the influence of the acid–base properties of the surface of the solid on the electronic structure of the adsorbed compound[11]. It is assumed that the allyl compound on a surface with acid properties (bismuth molybdate) is cationic and readily combines with the surface oxygen to form an unsaturated aldehyde. On the other hand, basic surfaces (manganese and zinc oxides) lead to the formation of free radicals.

On the basis of the results of the oxidation of propene labelled with radioactive carbon in the methylene group, it has been concluded[100] that hexa-1,5-diene is formed in the presence of a silver catalyst via an intermediate compound of the allyl type. However, the lack of data for the isomerisation of propene, the rates and mechanism of which depend on the type of catalyst[101], casts doubt on the validity of the above conclusion. In the case of rapid isomerisation, the mechanism presupposing the formation of a π-complex operates. A choice can apparently be made between these mechanisms on the basis of the results of the oxidative dehydrodimerisation of propene labelled with radioactive carbon and deuterium in different positions.

Another important factor in the mechanism of oxidative reactions involves the question of which forms of oxygen are responsible for the conversion of the hydrocarbon via a particular pathway. In the presence of many oxide catalysts the oxidative dehydrogenation[103,104] and partial oxidation[105,106] reactions of lower olefins, for example, proceed via an oxidation-reduction mechanism involving the oxygen of the surface layer of the catalyst. On the other hand, in the complete oxidation of the same hydrocarbons, the associative mechanism, which does not rule out the involvement in the reaction of forms of oxygen different from that of the oxide, makes an appreciable contribution.

Table 3. Comparison of the rates of the catalytic reaction and of the reduction and oxidation of the bismuth–tin oxide catalyst in the stationary state[107].

Reaction	Temp., °C	Mixt. compn., vol.%		$10^{-16}r$, molecules $m^2 s^{-1}$			
		C_3H_6	O_2	C_3H_6	O_2	C_6H_{10}	CO_2
Catalysis	450	0.67	0.38	1.8	5.16	0.29	4.05
Reduction	450	0.70	—	1.49	—	0.40	2.01
Oxidation	450	—	0.40	—	3.59	—	—
Catalysis	500	0.66	0.40	3.25	8.45	0.62	6.09
Reduction	500	0.67	—	2.45	—	0.65	3.52
Oxidation	500	—	0.38	—	3.69	—	—

Using the data of Gamid-zade et al.[107], the rates of the oxidative dehydrodimerisation and extensive oxidation of propene under the conditions of simultaneous and separate interactions of propene and oxygen with the bismuth–tin oxide catalyst are compared in Table 3. The satisfactory agreement between the rates of formation of diallyl in the catalytic and reduction processes shows that the oxide-hydrodimerisation proceeds via a multistage mechanism involving the separate interaction of the reactants with the catalyst surface. The main bulk of carbon dioxide is also formed from the catalyst oxygen. At the same time, the significantly higher rates of the total oxidation of propene in the catalytic process compared with the rates in the reduction process show that, under the conditions investigated, there is a considerable contribution of the combined mechanism, which diminishes with increase of temperature. It is important to note that the rates of the catalytic reaction and its individual stages have been compared for a catalyst in the stationary state. Under the conditions investigated, the stationary surface area was reduced by 70–80% and was characterised by the absence of weakly bound oxygen (Fig. 4).

The oxygen in the surface of the bismuth–tin oxide catalyst is apparently also involved in the oxidative dehydroaromatisation of propene to benzene. This was shown in a study by a pulsed method of the interaction of propene with the catalyst in the absence of gaseous oxygen[40,108].

The operation of the oxidation-reduction mechanism may be expected on the bismuth–phosphorus[109] and bismuth–titanium[110] oxide catalysts, for which a qualitative correspondence between the catalytic and reduction processes has been established. In the interaction of propene with the individual oxides of bismuth[12,111–113], tin[40,80,113], zinc[113], and indium[113] the same products are obtained (diallyl, benzene, and carbon dioxide) as under the conditions of the catalytic reaction. These findings show that a definite proportion of the products of the oxidative dehydrodimerisation and total oxidation of propene are formed with direct participation of the oxygen of the above catalysts. However, the final conclusion concerning the validity of the oxidation-reduction mechanism or lack of it could be arrived at only on the basis of a comparison of the rates of the catalytic reaction and the separate interactions of the components of the reaction mixture with the catalyst having the stationary composition, as has been done for the bismuth–tin oxide catalyst[107]. Furthermore, this procedure would permit a test, to some extent, of the possibility of the occurrence of the reaction via a heterogeneous-homogeneous mechanism.

It is known[114] that many catalytic reactions, initiated on the surfaces of solids and then transferred to the gas phase, proceed via a radical-chain mechanism. In particular, it has been suggested[115] that both reactions occur simultaneously in the oxidation of propene on certain oxide catalysts. One of these leads to the formation of acrolein via a purely heterogeneous mechanism. The second, homogeneous reaction is initiated by a surface hydroperoxide, formed via the addition of molecular oxygen to the allyl compound.

On this basis, one can assume that hexa-1,5-diene is formed via the gas-phase dimerisation of intermediate radical species (for example, allyl radicals) generated by the catalyst surface. The occurrence of oxidative dimerisation and aromatisation of propene becomes appreciable at high temperatures in excess of 450 °C. Under these conditions, there is a possibility of a weakening of the allyl–catalyst bond and of an increase of the probability of the transfer of allyl to the gas phase. This is supported by the detection of the allyl radical in the gas phase over zinc oxide and manganese oxide catalysts[98,99], which was mentioned above. However, data concerning the involvement of the allyl radical in the formation of diallyl have not so far been obtained. Furthermore, the allyl radicals generated by a pyrolytic procedure exhibit an absolute indifference to the

nature of the catalyst. When they interact with catalysts of the oxidehydrodimerisation and partial and extensive oxidation of olefins, only acrolein is formed[116]. The equality of the rates of the catalytic and reduction processes established for the bismuth–tin oxide catalyst also constitutes evidence against the heterogeneous-homogeneous mechanism, because the surface reduction of oxides usually proceeds via a heterogeneous mechanism[117].

Together with diolefins, aromatic hydrocarbons are formed on many of the known catalysts: benzene is formed from propene and xylenes are formed from butenes[25,93]. The relative content of aromatic hydrocarbons in the reaction products depends both on the chemical nature of the catalyst and on the reaction conditions. It has been noted that, on individual bismuth[12,13], thallium[18], and lead[15–17] oxides, hexa-1,5-diene is formed preferentially, whereas on catalysts of the type of zinc oxide[11], tin dioxide[11,40], and bismuth phosphate[25], the formation of aromatic hydrocarbons is more appreciable. An increase of the yield of the latter with a simultaneous decrease of selectivity with respect to diolefins is also promoted by an increase of contact time[45,84], which shows that hexa-1,5-diene is converted into aromatic hydrocarbons in successive stages.

It has been suggested[45,93] that benzene is formed via the oxidative dehydrogenation of hexa-1,5-diene to hexatrienes, the conversion of hexatrienes into cyclohexa-1,3-diene, and oxidative dehydrogenation of the latter to the aromatic compound. This mechanism is supported by the results of the oxidation of hexa-1,5-diene and cyclohexa-1,3-diene, which are converted respectively into a mixture of benzene with hexa-1,3,5-triene and benzene[93]. Furthermore, in the presence of many catalysts[12,13,22], the products include, together with diallyl and benzene, also cyclohexa-1,3-diene, which is the only cyclic diolefin detected.

Trimm and coworkers[84,85] put forward a somewhat simplified mechanism for the aromatisation of hexadienes having excluded from consideration the hexatriene formation stage. Having failed to detect hexatrienes among the reaction products, the authors suggest that the hexadiene localised on the catalyst surface is converted into cyclohexa-1,3-diene, which can then migrate to the catalytic centre, ensuring the formation of benzene. However, the absence of trienes from the reaction products cannot serve as an adequate justification for their exclusion from the formal reaction mechanism. One can assume that, by virtue of their high reactivity, the hexatrienes formed undergo readily and rapidly thermal "cycloisomerisation" to cyclohexadienes[118], as happens in the C_6-dehydrocyclisation of paraffinic hydrocarbons[2].

Indeed, Vaabel' et al.[119,120], who studied in detail the reactions of hexa-1,5-diene, cyclohexene, cyclohexa-1,3-diene, and benzene in the presence of the bismuth–tin oxide catalyst, showed that the hexatriene formed under the conditions of the oxidative dehydrodimerisation of propene cyclises and aromatises at a high rate. They also established that the pathway followed in the cyclisation of hexa-1,5-diene via cyclohexene cannot be the main one.

The facts described suggest that the oxidative dehydroaromatisation of olefins is a complex consecutive reaction, whose mechanism can be represented as follows in the case of propene:

$$\text{propene} \xrightarrow{1} \text{hexa-1,5-diene} \xrightarrow{2} \text{hexa-1,3,5-triene} \xrightarrow{3}$$

$$\text{cyclohexa-1,3-diene} \xrightarrow{4} \text{benzene}.$$

All the oxidative dehydrogenation stages (*1*, *2*, and *4*) are catalytic, while the cyclisation stage (*3*) is thermal, by analogy with the dehydrocyclisation process[2].

III. OXIDATIVE DEHYDRODIMERISATION OF OTHER HYDROCARBONS WITH MULTIPLE BONDS

The oxidative dehydrodimerisation and aromatisation of lower olefins is a special case of the more general type of reactions, which apparently extend to a wide range of compounds containing multiple bonds.

Reports of the vapour-phase heterogeneous-catalytic dehydrodimerisation of a number of compounds have been published mainly in the patent literature. Thus American investigators have patented[44,121,122] a procedure, which is feasible in principle, for the oxidative dehydrodimerisation of substances having the general formula YCRR'H to compounds of the type $(YCRR')_2$, where $Y = CH_2=CH$, Ph, CN, COOH, COOR, CO, or $CH_2=CX$ (X = halogen, alkyl, or allyl) and R and R' = hydrogen, C_1–C_6 alkyl groups, or aryl groups. The oxides of bismuth, chromium, iron, and a number of other elements, promoted by alkali metal compounds, have been suggested as catalysts. However, specific example of the processes described in the patents are confined to propene.

Among the substances enumerated above, alkyl derivatives of aromatic compounds have been studied in greatest detail. In particular, a relatively large number of patents are devoted to the selection of catalysts and the development of methods for the oxidative dehydrodimerisation of toluene to bibenzyl and stilbene.

Catalysts which are effective in the oxidehydrodimerisation reactions of lower olefins are also active in the oxidative dehydrocoupling of mono- and di-substituted benzenes. These include catalysts based on bismuth and antimony oxides with promoting additives[34,123], lead oxide on a carrier[15,16], the bismuth–tin oxide catalyst[124,125], the bismuth–iron oxide catalyst[125], and a number of others. The activity of noble metals and their oxides, hydroxides, and halides deposited on a zeolite or an aluminosilicate in these processes has also been reported[126].

The catalytic properties of the bismuth–tin oxide system have been studied in greatest detail. It has been shown[127] that the $Bi_2Sn_2O_7$ phase is formed in the course of the preparation of the catalyst, its content increasing with increasing heat-treatment temperature. At the same time the activity of the catalyst in the oxidative dehydrodimerisation of toluenes is found to increase. However, the bismuth pyrostannate phase is unstable in the atmosphere of the reaction medium at high temperatures. At 600 °C it is converted into the α-Bi_2O_3, γ-Bi_2O_3, and $Bi_{12}SnO_{20}$ phases. The bismuth–tin oxide catalysts retain a constant activity only in the course of the first three hours of operation, after which the activity and selectivity of the catalyst decrease slowly owing to coke deposition. After regeneration with air, the catalysts fully recover their properties[128].

The maximum selectivity in the formation of bibenzyl and stilbene (45%) is observed at 500 °C. With increase of temperature, the selectivity falls due to the oxidative dealkylation of toluene to benzene. With increase of the conventional contact time and the oxygen/toluene ratio in the mixture, the selectivity with respect to stilbene increases and that with respect to bibenzyl falls. These results show that stilbene is formed from bibenzyl via its oxidative dehydrogenation[128].

Oxidative dehydrodimerisation reactions of alkyl derivatives of aromatic hydrocarbons proceed much more selectively in the presence of molecular iodine. The latter arrives on the catalyst layer together with oxygen as part of the initial mixture[129–131] or is formed directly in the reaction zone as a result of the action on the catalyst by the components of the

reaction mixture, as happens in the familiar catalyst of the Shell Company (a mixture of LiI, LiOH, and Li_2SO_4 melts)[132]. For example, when melts of lithium and lead iodides are used, it is possible to achieve the dehydrocoupling of toluene to stilbene, of toluene and propene to naphthalene, and of isopropylbenzene to *p*-terphenyl[133].

It has been suggested in a number of patents[16,122,134,135] that hydrogen split off in the dehydrodimerisation of alkyl derivatives of aromatic hydrocarbons be combined with the oxygen of the metal oxides. Among the latter, mention is made of the individual and deposited oxides of bismuth, cadmium, lead, and arsenic. During the reaction, the oxides are reduced and periodic reoxidation is necessary.

Benzene apparently undergoes vapour-phase oxidative dehydrodimerisation with much more difficulty. There has been only one report of a study[126] in which noble metals were used as catalysts for this purpose. There is absolutely no information about the ability of oxides to catalyse the oxidative conversion of benzene into biphenyl. This may be explained by the fact that the dissociation energy of the C–H bond in the benzene ring (102 kcal mol^{-1}) is significantly higher than in the methyl groups of toluene and propene (83 kcal mol^{-1}).[136] In other words, the formation of phenyl radicals $C_6H_5^{\bullet}$ is energetically less favourable than that of benzyl radicals $C_6H_5CH_2^{\bullet}$, which are believed[137] to behave as intermediates in the oxide-hydrodimerisation of toluene. Furtherfore, as a consequence of the delocalisation of the π-electronic charge of the ring or the C=C bond with participation of a partially vacant orbital, the benzyl and allyl radicals exhibit an increased stability[138], which should also favour their dimerisation. The formation of the benzyl radical on the surface of zinc oxide in the adsorption of toluene has been demonstrated spectroscopically[139].

The high reactivity of lower olefins and toluenes in oxidative dehydrocoupling reactions compared with benzene indicates the possibility of the involvement in such reactions of a large number of hydrocarbons having a mobile hydrogen atom in the α-position relative to the unsaturated bond. Here one should expect the occurrence of the following consecutive stages: the abstraction of the above hydrogen atom following the adsorption of the hydrocarbon on the surface of the appropriate catalyst, dimerisation of the molecular fragments, oxidative dehydrogenation of the dimer, and, its subsequent cyclisation and aromatisation, provided that this is allowed by the structure of the compound formed.

IV. CONCLUSION

The study of heterogeneous-catalytic dehydrodimerisation and cyclisation reactions in the presence of molecular oxygen was begun comparatively recently and so far embraces a limited number of catalysts and a narrow range of hydrocarbons. Certain aspects of the conversion of substances on the surface of catalysts and the mechanisms of the action of the latter remain unelucidated. Nevertheless, the results obtained show that these reactions are fairly complex and represent a set of consecutive stages.

Oxidative dehydrodimerisation reactions of hydrocarbons are accompanied by a number of side reactions involving total and partial oxidation. The discovery of the principal features of reactions of the above type is therefore of interest for the theory of oxidative catalysis as a whole.

By virtue of the involvement of oxygen, oxidative dehydrodimerisation processes differ from the dehydrocyclodimerisation reactions of lower paraffins and olefins[1], which have been thoroughly investigated and have much in common with oxidative heterogeneous catalytic processes. In the first place the common features of their mechanisms should be noted. As shown in this review, the oxidative dehydrodimerisation of lower olefins on oxide catalysts proceeds via a mechanism involving the separate interaction of the reactants with the surface of the catalyst. A considerable proportion of the total oxidation products are formed via a combined mechanism, whose contribution to the overall rate of reaction diminishes with increase of temperature. The conversion of olefins on many oxide catalysts of the partial oxidation reaction proceeds similarly[103–106].

The similarity of the mechanisms is also manifested in the reaction kinetics. Both in the partial oxidation[91] and oxidative dehydrodimerisation[88] of lower olefins, the rate-limiting stage involves the dissociation of the C–H bond in the allyl position. Furthermore, with increase of the oxygen content in the reaction mixture, the selectivity with respect to the mild reaction product (diallyl) increases and that with respect to the extensive oxidation products increases[89], as has been observed in the oxidation of ammonia and a number of organic substances[140,141].

An increase of the binding energy of the surface oxygen on oxide catalysts leads to a decrease of the rate and an increase of the selectivity of the partial oxidation[60,61]. Similar relations have been established for the oxidehydroaromatisation of propene on simple oxides[11]. As a consequence of this, the mode and rate of conversion of olefins on dehydrodimerisation catalysts depend on the strength of binding of oxygen and the degree of surface coverage by the latter. The features observed for the bismuth–tin oxide catalyst show consistently[69,107] that a necessary condition for the selective action of the catalyst is the absence of weakly bound oxygen from its surface. In the stationary state the surface of the catalyst is characterised by a high degree of reduction and the presence of energetically homogeneous oxygen with a relatively high binding energy (90 kcal mol^{-1}). It is of interest to note that this quantity is close to the binding energy of oxygen in the stationary state on a number of selective partial oxidation catalysts[142,143].

Finally, one can postulate that the binding energy of oxygen is not the only factor determining the selectivity of oxide catalysts in oxidative dehydrodimerisation of olefins. In order to obtain a high selectivity in the presence of strongly bound oxygen, specific activation of the hydrocarbon molecule is apparently necessary, as in the mild oxidation processes[106]. It is not fortuitous that the bismuth–tin oxide catalyst, which consists of a combination of metal cations on which highly reactive allyl compounds are formed and stabilised, catalyses effectively the oxidehydrodimerisation of propene. The extension of the range of catalysts investigated will permit a comparison of the selectivities with the binding energies of oxygen and will provide a more unambiguous answer to this question.

The factors enumerated permit the conclusion that the oxidative dehydrodimerisation of unsaturated hydrocarbons is a typical example of the large class of heterogeneous-catalytic reactions with participation of molecular oxygen and that the principal relations determined previously for partial and total oxidation reactions of hydrocarbons are applicable to this process. This must be taken into account in selecting catalysts.

At the same time there is a considerable difference in the approaches to the solution of the problem of the selection of catalysts for the oxidative dehydrodimerisation and partial oxidation of olefins. This follows from the opposite variation of the activities of the oxide catalysts in these reactions with

their acid–base properties[30,70–72] and is associated with the type of conversion of the allyl type intermediates. The oxidation of the latter to unsaturated aldehydes requires the presence on the catalyst surface of Lewis acid centres with an enhanced strength and of electrophilic oxygen, which is achieved by combining amphoteric and acid oxides[79]. On the other hand, effective dimerisation requires weak acid centres and the absence of electrophilic oxygen. Such properties are characteristic of the oxides of weakly basic and amphoteric elements, combinations of which should apparently be sought as a basis for catalysts of the oxidative dehydrodimerisation of unsaturated hydrocarbons. The majority of the catalysts discussed in this review are consistent with this postulate.

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The Nature of the Primary Photochemical Step in Spiropyrans

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The mechanisms of the photocolouring reactions of spiropyrans are considered and the vibrational mechanism for the dissociation of the $C_{(2)}$-O bond in spiropyrans is analysed taking into account the relative positions of the π,π^* and n, π^* levels. The nature of the photochemically active state in spiropyrans has been established by examining the electronic nature of the low-lying excited states in organic molecules with heteroatoms. A mechanism is proposed for the photocolouring of spiropyrans, which explains the dependence of the efficiency of the $C_{(2)}$-O bond dissociation reaction in spiropyrans on their structure. The bibliography includes 63 references.

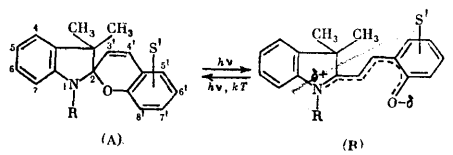
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I. INTRODUCTION

The photochromic transformations of spiropyrans (SPP) are based on a reversible intramolecular photochemical reaction. In view of the enormously wide variety of structures existing in spiropyrans[1] and the ease with which the coloured form of spiropyran can be detected, the above compounds constitute a convenient model for investigating the nature of the primary photochemical step in organic molecules with heteroatoms and its dependence on the medium and the nature of the molecule. At the same time one should note that, by virtue of their unique properties, the photochromic spiropyrans are extremely promising for practical application in various branches of science and engineering[1-4].

The overall process involving photochromic transformations of spiropyrans belonging to one of the best known subclasses—spiropyrans of the indoline series—can be represented schematically as follows[1]:



(A) (B) (1)

In the initial form of SPP the indoline and benzopyran fragments of the molecule are linked by the spirocarbon $C_{(2)}$ atom with tetrahedral sp^3-hybridisation of atomic orbitals; these

fragments are therefore orthogonal relative to one another. This was confirmed by the X-ray diffraction analysis of a single crystal of 3,3-dimethyl-8′-nitro-1-phenylspiro[indolino-2,2′-(2′*H*-1-benzopyran)].[5] Henceforth 1,3,3-trimethylspiro[indolino-2,2′-(2′*H*-1-benzopyran)] will be designated by SP_1 (see Table). The orthogonality of the indoline and benzopyran fragments of the SPP is responsible for the orthogonality of the π-electron systems of these fragments and hence justifies the assumption, to a first approximation, that the properties of the indoline and benzopyran components of the SPP are independent[1].

The coloured state of the SPP obtains following the heterolytic dissociation of the $C_{(2)}$–O bond when the hybridisation of the spirocarbon atom changes to the sp^2-type[1]. This results in the formation of planar molecules with delocalised π electrons of the indoline and benzopyran components, giving rise to an intense absorption band in the visible part of the spectrum. Merocyanine dyes can serve as a model of the coloured form of spiropyran[1]. The complex dependence of the form of the long-wavelength absorption bands of the coloured form of SPP with an electron-accepting substituent in the benzopyran component (for example, SP_2 and SP_3) on the solvent and temperature can be explained by the existence of a series of stereoisomers of form B.[1,6–12] In view of the small height of the energy barrier to the transition between the stereoisomers at room temperature, thermodynamic equilibrium is established between them in solution in less than 10^{-7} s.[6]

In a number of studies devoted to the photochromic transformations of SPP at low temperatures[8,12] and at room temperature (with the aid of laser nanosecond spectroscopy)[6,9,10], it has been established that the formation of the coloured forms of SP_2 and SP_3 proceeds via a stage involving the formation of an unstable isomer X, which is a molecule of the SPP with a ruptured $C_{(2)}$–O bond but with an unaltered molecular geometry.[12]

The coloured form of the SPP is formed when the SPP is acted upon not only by ultraviolet light at a wavelength in the region of the absorption spectrum of the initial form of the SPP but also under the influence of ionising radiation[1]. Fairly extensive data concerning the mechanism of the photocolouring of the SPP under the influence of ultraviolet light in the wavelength range 300–405 nm (this region contains the first and second absorption bands of the initial form of the SPP due to electronic transitions of the π–π* type which are localised mainly in the benzopyran component of the SPP[1]) have now accumulated, while the number of studies devoted to the photolysis of SPP under the influence of light with $\lambda < 300$ nm is so far small[1,9,13]. Analysis and interpretation of the results of the study of the photolysis of SPP by light with $\lambda < 300$ nm is complicated by the fact that, in addition to the high-energy electronic transitions localised mainly in the benzopyran component of the SPP, light at this wavelength excites also the electronic transitions in the indoline component. On the other hand, the redistribution of the electronic excitation energy of the indoline component via different channels (emission and dissipation within the indoline component, transfer to the benzopyran component) has been little investigated[1]. It has been suggested[13] that, transfer of the electronic excitation energy from the indoline to the benzopyran component of the SPP may cause the production of form B. In this sense the photocolouring of the SPP by light absorbed by its indoline component is apparently related to the photosensitised colouring of SPP.

The main question concerning the mechanism of the formation of the coloured form of SPP is how the electromagnetic radiation energy absorbed by the benzopyran component of the SPP is transformed into the $C_{(2)}$–O bond dissociation energy[1]. Tasks of practical importance, involving the discovery and explanation of the laws governing the variation of the spectral-kinetic characteristics of the photochromic transformations of spiropyrans as a function of their structure and external conditions, are closely related to the solution of this problem.

The quantum yields of the photocolouring ($\phi_{AB}^{u.v.}$) and photodecolorisation ($\phi_{BA}^{u.v.}$) of spiropyrans A with different substituents under the influence of ultraviolet light.

Spiropyran	Substituent	Solvent	*t*, K	φ_{AB}^{313} (φ_{BA}^{313})	φ_{AB}^{365} (φ_{BA}^{365})	Refs.
SP_1	1-CH_3	Hexane	173	0.1 (0.001)	—	[1]
SP_2	1-CH_3-5′,6′-benzo	Hexane	173	0.06 (0.01)	—	[1]
		Polystyrene	77	0.02	0.02	[31, 39]
SP_3	1-CH_3-6′-NO_2	Ethyl acetate	293	0.40	0.60 (0.01)	[38]
		Toluene	293	—	0.76 (0.0)	[36]
		Polystyrene	77	0.05	0.1	[31, 39]
SP_4	1-C_6H_5-6′-NO_2	Ethyl acetate	293	0.30	0.60 (0.0)	[38]
		Polystyrene	77	0.03	0.06	[31, 39]
SP_5	1-CH_3-6′-NO_2-7′-OCH_3	Ethyl acetate	293	—	0.35 (0.02)	[38]
SP_6	1-C_6H_5-6′-NO_2-7′-OCH_3	Ethyl acetate	293	—	0.35 (0.01)	[38]
SP_7	1-CH_3-6′-NO_2-7′-OC_3H_7	Ethyl acetate	293	—	0.25 (0.09)	[38]
SP_8	1-CH_3-6′-NO_2-8′-OCH_3	Ethyl acetate	293	0.30	0.45 (0.08)	[38]
		Toluene	288	—	0.59 (0.0)	[1]
		Dioxan	288	—	0.43	[1]
SP_9	1-CH_3-5′-Br-6′-NO_2-8′-OCH_3	Dioxan	288	—	0.44	[1]
SP_{10}	1-C_6H_5-6′-NO_2-8′-OCH_3	Ethyl acetate	293	0.10	0.45 (0.07)	[38]
SP_{11}	1-CH_3-6′-NO_2-8′-CH_2-CH_2	Ethyl acetate	293	—	0.55 (0.0)	[38]
SP_{12}	1-C_6H_5-6′-NO_2-8′-CH_2-CH-CH_2	Ethyl acetate	293	—	0.55 (0.05)	[38]
SP_{13}	1-C_6H_5-6′-NO_2-8′-Cl	Ethyl acetate	293	—	0.55 (0.0)	[38]
SP_{14}	1-C_6H_5-6′-NO_2-8′-Br	Ethyl acetate	293	—	0.45 (0.01)	[38]
SP_{15}	1-CH_3-5′,7′-di-Cl-6′-NO_2	Dioxan	288	0.47	0.58 (0.015)	[1]
		Toluene	293	0.45 (0.0)	0.55 (0.0)	[1]
SP_{16}	1-CH_3-5′,6′-di-NO_2-8′-OCH_3	Dioxan	288	—	0.23 (0.04)	[1]
SP_{17}	1-CH_3-7′-NO_2	Ethyl acetate	293	—	0.17 (0.04)	[38]
SP_{18}	1-C_6H_5-8′-NO_2	Ethyl acetate	293	—	0.13 (0.00)	[38]
		Polystyrene	77	0.02	0.03	[31, 39]
SP_{19}	1-CH_3-6′-Cl-8′-NO_2	Ethyl acetate	293	—	0.05 (0.00)	[38]
SP_{20}	1-C_6H_5-6′-Cl-8′-NO_2	Ethyl acetate	293	—	0.05 (0.00)	[38]
SP_{21}	1-CH_3-4,5-benzo-6′-NO_2	Ethyl acetate	293	—	0.025 (0.015)	[38]
SP_{22}	1-CH_3-6,7-benzo-6′-NO_2	Ethyl acetate	293	—	0.015 (0.010)	[38]
SP_{23}	1-CH_3-6′-CHO	Ethyl acetate	293	0.25	0.05 (0.01)	[38]

Note. The radiation yields G_B of the coloured forms of the spiropyrans SP_2, SP_3, SP_4, SP_8, and SP_{18} in polystyrene at −77 K under the influence of γ-rays are respectively 0.07, 0.4, 0.25, 0.06, and 0.13.

The aim of the present review to analyse the existing ideas concerning the mechanism of the photocolouring of spiropyrans and their generalisation on the basis of the analysis of the nature of the electronically excited states of spiropyrans.

II. THE VIBRATIONAL MECHANISM OF THE DISSOCIATION OF THE $C_{(2)}$–O BOND

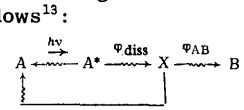
Studies have been made[13,14] on the dependence of the relative quantum yield of the fluorescence of unsubstituted chromenes and SP_2 as well as the relative fluorescence yield (ν) of SP_3 in trimethylpentane at 77 K on the wavelength of the exciting light λ_e. By analysing the vibrational absorption bands of chromenes and SP_2, the authors[13,14] established that the relative fluorescence quantum yield of the above compound decreases significantly with excitation of increasingly higher vibrational levels and that an even greater decrease of the fluorescence yield is observed when chromenes and SP_2 are irradiated with light at the wavelength

corresponding to the second absorption band. The decrease of the relative fluorescence quantum yield is explained[13,14] by the competition between the photochemical $C_{(2)}$–O bond dissociation process and the internal transition from the excited to the zero-point vibrational level, from which there is a radiative transition to the ground state.

The finding that the competition of the photochemical process is particularly pronounced on excitation of sequences of vibrations at the frequencies corresponding to the antisymmetric vibrations of the –C–O–C– group is consistent with this explanation. Three possible explanations of the vibrational mechanism of the photocolouring of SPP have been proposed[13,14]. The first applies to the case where the potential energy curve for the first excited singlet state has a "small" minimum, so that the $C_{(2)}$–O bond is ruptured after the excitation of only the first vibrational level of the S_1 state. In the second case it is assumed that the potential energy curve for an unbound excited state intersects the potential energy curve for the S_1 state near its first vibrational level. The third explanation can be used when the $C_{(2)}$–O bond is dissociated in the triplet state and the absorption of even only one vibrational quantum is sufficient for the transition of the molecule from the S_1 state to the T_0 state.

For the indoline SPP with a nitro-group in the 6′-position, a study was made of the dependence of ν on λ_e in 3-methylpentane at 77 K. The nature of this dependence is different than for the fluorescence quantum yields of chromenes and SP_2. The value of ν corresponding to SP_3 irradiated with light at $\lambda_e = 372.5$ nm was assumed to be unity; with decrease of λ_e to 323 nm, it diminishes slightly—to ~0.8; a further decrease of λ_e down to 269 nm no longer altered the above quantity. In order to account for such dependence of ν on λ_e, the authors[13] invoke the transfer of energy from the indoline component of the molecule to the benzopyran component in addition to the vibrational mechanism of the dissociation of the $C_{(2)}$–O bond. They believe that the constancy of ν starting with $\lambda = 323$ nm can be explained by the fact that at $\lambda < 323$ nm the indoline component of the molecule begins to absorb; however, since the phosphorescence of the indoline component itself is not then observed, it is suggested that the electronic excitation energy is transferred from the indoline to the benzopyran fragment, as a result of which a constant value of ν for the benzopyran component is established. In the absence of energy transfer from the indoline fragment of the molecule, ν for the benzopyran component should decrease with diminution of λ_e from 372.5 to 323 nm by an amount greater than that observed as a consequence of the competition of the photochemical $C_{(2)}$–O bond dissociation process[13].

Thus, ν for SP_3 decreases by 20% when λ_e falls from 372.5 to 269 nm, while the quantum yields of the photocolouring of this SPP under the influence of light at wavelengths of 365 and 313 nm (in 1-propanol-2-propanol mixture at 153 K) are 0.6 and 0.3 respectively[8]. It follows from these results that, firstly, the quantum yield of the photocolouring reaction (ϕ_{AB}) and the quantum yield of the photochemical $C_{(2)}$–O bond dissociation reaction (ϕ_{diss}) are different quantities. In the general case it is necessary to take into account the possibility of the reverse process—the formation of the initial form A after the dissociation of the $C_{(2)}$–O bond, i.e. the photocolouring reaction must be represented schematically as follows[13]:



(2)

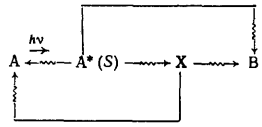
Secondly, the parallel variation of the quantum yield of the photocolouring and phosphorescence of SP_3 with λ_e shows that in this case the observed relations cannot be explained solely by vibrational mechanism of the $C_{(2)}$–O bond dissociation process and it appears that this mechanism cannot be the main mechanism of the photocolouring reaction ensuring the high values of ϕ_{AB} observed.

Indeed, the vibrational mechanism of the dissociation of the $C_{(2)}$–O bond does not take into account the nature of the electronic transition excited by light and the specific features of the electronic transition determine the efficiency of the photophysical and photochemical processes in organic molecules with heteroatoms[15,16]. Since the nature of the electronic transition actually helps to elucidate the dependence of the efficiency of intramolecular processes on the molecular structure, the vibrational mechanism of the photocolouring reaction is unsatisfactory. One should also note that, whereas in the case of chromenes the photochemical process may be the only one competing with the internal transition, on passing to the SPP with an indoline fragment, one cannot rule out the possibility also of other channels leading to a redistribution of the electronic excitation energy apart from the photochemical processes and fluorescence; in particular, one can postulate the occurrence of conformational vibrations of the molecule as a whole. The study of the vibrational mechanism of the photocolouring of the SPP should not therefore be limited to the measurement of the fluorescence or phosphorescence quantum yield; the parallel measurement of the photocolouring yield is also necessary.

III. THE RELATIVE POSITIONS OF THE LOWEST π,π^* AND n,π^* LEVELS AND THE MECHANISM OF THE PHOTOCOLOURING OF SPIROPYRANS

An attempt has been made in a number of studies[6,8–11,17–26] to explain the dependence of the photocolouring of the SPP on their structure by considering the relative positions of the lowest electronically excited states of the SPP[11,26] and also by determining the states in which the $C_{(2)}$–O bond dissociates and form B is produced[6,8–11,17–25]. The majority of these studies were mainly devoted to the elucidation of the involvement of triplet states in the photochemical colouring of the SPP. Studies have shown[18–20,22,27,28] that sensitised photocolouring due to the triplet–triplet transfer of energy from a triplet donor to the SPP is observed for all the SPP investigated, including SP_1 and SP_3. On the other hand, it was found[1,10] that the involvement of the triplet states in the direct photocolouring of the SPP is not observed for all SPP structures.

The spiropyrans SP_1 and 6′- or 7′-methoxy-SP_1 do not show an influence by oxygen on the photocolouring process[17] and exhibit neither phosphorescence[13,26] nor triplet–triplet absorption bands[8,17]. On this basis, one can assume that, on direct photoexcitation of SPP of this kind, the formation of form B takes place mainly from the excited singlet state and can be represented by the following scheme[10,11]:



(3)

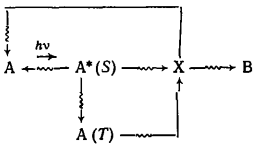
The involvement of the triplet states in the direct photocolouring of SP_3 is indicated by the presence of short-lived absorption bands due to the T_0–T_1 transition, the kinetics of the changes in which are correlated with the kinetics of the increase in the intensity of the absorption by the coloured form of the SPP[8,9,23,24]. Attempts have been made in a number of studies[21,25,28] to demonstrate the presence of the photochemically active (PCA) triplet state of the SPP with the nitro-group in the benzopyran part of the molecule by

investigating the kinetics of the photocolouring of the SPP in the presence of a triplet energy acceptor.

It has been established[21,25] that, in the presence of anthracene[25], 9-fluorenone, or benzil[21], the efficiency of the colouring of the SPP in solutions by light with $\lambda = 365$ nm is reduced. The authors of the above investigations believe that this is caused by the deactivation of the triplet PCA states of the SPP as a result of energy transfer from the SPP to the triplet energy acceptor. Calculations have shown that 83% of the coloured molecules are formed via the triplet states in the case of SP_8[25] and 20% in the case of SP_{15}[21].

However, it has been found[28] that the efficiency of the colouring of 8′-bromo-6′-nitro-SP_1 by light with $\lambda = 405$ nm is independent of the presence in solution of added anthracene (at a concentration up to 10^{-2} M). Furthermore, dissolved oxygen, which is an effective quenching agent for triplet states, does not exert an appreciable influence on the final yield of the coloured SPP molecules[1,8,21,28]. These results throw doubt on the possibility of explaining the observed decrease in the efficiency of the photocolouring of nitro-substituted SPP in terms of the quenching of their triplet states by triplet energy acceptors such as anthracene, 9-fluorenone, and benzil. If account is taken of the fact that the given compounds can show electron-accepting properties and hence there is a possibility of the phototransfer of an electron from the SPP[29–33], then one cannot rule out the probability of a chemical interaction between them and the SPP, which can lead to a decreased efficiency of the formation of coloured SPP molecules. When the SPP–anthracene system is irradiated with light at a wavelength of 365 nm, it is apparently necessary to take into account also the absorption of the initiating light by the molecules of anthracene itself.

Studies of the photocolouring and phosphorescence of SP_3 in polymeric matrices [polystyrene and poly(methyl methacrylate)] between room temperature and 75 K led to the conclusion that under these conditions the photocolouring process takes place to the extent of 100% via triplet states[20]. Thus, scheme (2) can be represented in the following general form for an SPP with a nitro-group:



(4)

As regards the electronic nature of the triplet state under consideration, the results of a number of studies[20,25,26,34,35] have shown that the triplet PCA state and the phosphorescent state of these SPP are the same triplet state of the π,π^* type. The measured energies of the triplet PCA and phosphorescence states can differ as a consequence of the influence of the medium and temperature[25]; furthermore, the dissociation of the $C_{(2)}$–O bond in the triplet state can occur at vibrational levels above the zero-point level, while emission takes place only from the zero-point vibrational level of the lowest triplet state. This may explain the fact that the triplet PCA level of SP_3 in poly(methyl methacrylate) lies above the phosphorescence level[20].

Thus analysis of the literature data shows that the photocolouring of the SPP with electron-accepting substituents in the benzopyran part can take place via the triplet state. Since the population of the lowest triplet state depends on the intercombination transition, the probability of which in heteroatomic molecules is very sensitive to the relative positions of the π,π^* and n,π^* levels[15,16,36], an attempt was made[26] to elucidate the qualitative dependence of the photochromic properties of the indoline SPP on the relative positions of the singlet and triplet π,π^* and n,π^* levels. A study was made[26] of the absorption and emission spectra of two groups of SPP. The first group consisted of SPP which are non-photochromic at room temperature (of the type of 6′-bromo-SP_1 and SP_2) and SPP with a nitro-group in the 7′-position of the naphthopyran component. The second group incorporated SPP with a pronounced photochromism at room temperature—SP_3 and SP_{23}. The authors determined the relative positions of the singlet and triplet levels of the π,π^* and n,π^* types. It was found that even if levels of the n,π^* type are present in the SPP of the first group, they lie above the $^1(\pi,\pi^*)$ level. For the SPP of the second group, at least one of the $^1(n,\pi^*)$ or $^3(n,\pi^*)$ levels lies between the $^1(\pi,\pi^*)$ and $^3(\pi,\pi^*)$ levels.[26] This should increase the probability of an intercombination transition for the SPP of the second group by 2–3 orders of magnitude compared with the first group[26].

On the basis of the results, it has been suggested[26] that the photochromism of the SPP at room temperature is closely related to the intercombination transition and that the colouring of the SPP with a distribution of π,π^* and n,π^* levels of the kind found, for example, in SP_3 takes place mainly via the triplet state. The observed dependence of the photochromic properties of the SPP on the relative positions of the π,π^* and n,π^* levels can be used, according to the authors[26], to explain the dependence of the photochromic properties of the SPP on their structure. This approach was also used in a study[11] of the photochromism of the SPP of the phenanthridine and diazapyrene series.

Despite the fact that the authors[11,26] were able to explain satisfactorily the dependence of the photochromic properties of the SPP on their structure, we believe that their findings are not general and do not reflect the fundamental processes responsible for the photochromism of the SPP. Indeed, the dissociation of the $C_{(2)}$–O bond is primarily an electronic process, which hardly depends on the temperature of the surrounding medium. However, the stability of the coloured form of the SPP is independent of this temperature. In the case of 6′-bromo-SP_1 and SP_2 a decrease of temperature results in their being photocoloured with an efficiency comparable to that of the photocolouring of SP_3 and SP_{23}.[1]

Apart from this, the mechanism proposed[26] for the photocolouring of the SPP does not take into account, like the vibrational mechanism of the dissociation of the $C_{(2)}$–O bond, the specific features of the electronic states in which the $C_{(2)}$–O bond is dissociated. This mechanism does not therefore permit an explanation of the change in ϕ_{AB} for the SPP as the nitro-group moved from the 6′-position to the 7′- or 8′-position or following the introduction into the benzopyran component of yet another substituent, in addition to the nitro-group; as noted above, within this series of the SPP there is a fairly considerable change in the contribution of the colouring process involving the triplet state. Furthermore, ϕ_{AB} exhibits an appreciable sensitivity also to λ_e.[1]

It is also noteworthy that the positions of the n,π^* levels are usually determined very approximately[36] in view of the low intensity of the band due to the n,π^* transitions and the superposition on the latter of the significantly more intense band of the π–π^* transitions. For example, the following sequence of low-lying excited levels has been determined for SP_3 in toluene: $S_0 < {}^3(\pi,\pi^*) < {}^3(n,\pi^*) < {}^1(\pi,\pi^*) < {}^1(n,\pi^*)$ while in another study[25] the following sequence was obtained for SP_8: $S_0 < {}^3(\pi,\pi^*) < {}^3(n,\pi^*) < {}^1(n,\pi^*) < {}^1(\pi,\pi^*)$. Therefore the rate of the intercombination transition for SP_8 should apparently be not lower than the rate of the intercombination transition for SP_3 and, according to the postulates developed

by Belaits and Platonova[26], the value of ϕ_{AB} for SP_8 should be not less than for SP_3. However, in reality the values of ϕ_{AB} for these SPP in toluene at room temperature under the influence of light with $\lambda = 365$ nm are 0.59 for SP_8 and 0.76 for SP_3.[1]

Thus the mechanism of the photocolouring of the SPP proposed on the basis of the consideration of only the intercombination transition and the SPP does not reflect, like the vibrational mechanism of the dissociation of the $C_{(2)}$–O bond, the entire specific features of the primary photochemical step in the photochromic transformations of the SPP.

IV. THE PHOTOCHEMICALLY ACTIVE STATE OF SPIROPYRAN AND THE MECHANISM OF THE DISSOCIATION OF THE $C_{(2)}$–O BOND

The photochemically active state of spiropyran is an excited state in which the $C_{(2)}$–O bond is dissociated. Heiligman-Rim et al.[12] explained for the first time the dissociation of the $C_{(2)}$–O bond by a redistribution of the electron density as a result of the excitation of the electronic transition in the benzopyran component of the SPP. They assumed that the mechanism of the photocolouring process consists of two stages: (1) the delocalisation of two σ electrons as a consequence of the redistribution of electron density on excitation of the electronic transition in the naphthopyran component of SP_2; (2) the change in molecular configuration.

Ring opening leads to the formation of a high-energy unstable merocyanine isomer (isomer X, see above), in which there is a partial retention of the configuration of the initial form of the SPP[12]. The authors[12] suggest that this configuration can be associated with the *cis*-isomer in which the steric repulsion is balanced by the attraction of nitrogen and oxygen atoms with unlike charges. This treatment of the photocolouring of the SPP appears to us reasonable on the whole; it has been confirmed, in particular, by the results of the study of the second stage of the process (see above).

The next stage in the development of ideas concerning the mechanism of the dissociation of the $C_{(2)}$–O bond was reached in studies[13,18,22,25,34,35,37] in which the absorption spectra of spiropyrans and compounds modelling the indoline and benzopyran components of the SPP were investigated. Their aim was to discover in which part of the SPP molecule a particular electronic transition is localised; hypotheses were put forward concerning the electronic nature of the photochemically active transition in the SPP.

The following models of the indoline component were adopted: indole[18,22], 2-hydroxy-1,3,3-trimethyl-2-phenylindoline[13], and 1,2,3,3-tetramethylindoline[25]. Different chromenes, for example, unsubstituted 2,2-diethyl-2*H*-chromene[22], 2,2-dimethyl-2*H*-chromene, or 2,2-dimethyl-5,6-benzo-2*H*-chromene[13], and substituted chromenes[25,34,35,37] were chosen as models of the benzopyran component. Comparison of the absorption spectra of the model compounds with those of solutions of the SPP permitted the conclusion that the electronic transitions, localised mainly in the indoline component of the SPP, give rise to absorption bands in the wavelength range $\lambda < 300$ nm[13,18,22,25]; mainly the absorption bands due to the electronic transitions in the benzopyran component of the SPP are distributed in the region $\lambda > 300$ nm[13,18,25,34,35,37].

However, although the absorption spectra of the model compounds make it possible to infer in which part of the SPP the particular electronic transition is largely localised, it has been noted[18,25] that the overall absorption spectra of compounds modelling the indoline and benzopyran components of the SPP agree with the absorption spectra of the SPP only to a first approximation and the difference between the intensities of the component bands is fairly large. This result shows that in practice the electronic systems of the indoline and benzopyran components of the SPP interact[1].

The electronic transition localised in the indoline component of the SPP is a π–π^* transition[15]. The following information is available about the nature of the transitions localised in the benzopyran component: in the spectrum of an SPP without substituents in the benzopyran fragment the absorption bands at 313 and 324 nm are caused by the π–π^* transition[13]; following the introduction of a bromine atom in the 6′-position of the SPP, a long-wavelength absorption band appears, whose dependence on the solvent polarity is characteristic of bands due to an n–π^* transition[22], while the extinction coefficient corresponds to a π–π^* transition. The author[22] denotes this transition as follows:

$$\overset{n\text{——}\pi^*}{\underset{\text{—O—}}{}}$$

emphasising thereby the electron-donating role in the latter of the oxygen heteroatom. In the SPP with a condensed benzene ring in the benzopyran component two π–π^* transitions correspond to two absorption bands in the range $\lambda > 300$ nm.[13,26]

When an electron-accepting substituent, for example, the nitro-group, is introduced into the benzopyran component of the SPP, an intense absorption band appears in the range 330–360 nm, which has been ascribed to the π–π^* transition[13,18,25,34,35,37]. It has been noted[22] that this band masks the absorption band due to the transition

$$\overset{n\text{——}\pi^*}{\underset{\text{—O—}}{}}$$

and n–π^* (the latter transition involves the nitro-group). It has been emphasised[13,18,25,34,35,37] that the excitation of the π–π^* transition in the benzopyran component with a nitro-group as a substituent leads to an increase of the positive charge on the oxygen heteroatom in the first excited singlet state.

The PCA transition in SPP with a nitro-group has been identified[22] as a n–π^* $\underset{\text{—O—}}{}$ transition. Bearing in mind that this transition involves charge transfer from the oxygen heteroatom to the benzene ring, the author[22] explained the observed decrease of ϕ_{AB} by a shift of the nitro-group from the 6′-position (*para*-position relative to the oxygen heteroatom) to the 7′- and 8′-positions. However, it is believed[25] that the PCA transition in SP_8 is a π–π^* transition and that the long-wavelength absorption band of the initial form of the given SPP corresponds to it. One should also note that the low-lying $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$ states of the SPP have been assigned[25] to states involving charge transfer from the oxygen heteroatom to the benzopyran ring.

A further development and generalisation of the ideas concerning the PCA transition in the SPP has been achieved in studies[38,39] where the dependence of the electronic absorption spectra of the initial forms and the ϕ_{AB} of the spiropyrans on their structure was investigated. A study has been made[38] of the spectral-kinetic characteristics of 20 indoline SPP under identical conditions. The absorption spectra in solution in ethyl acetate of a series of spiropyrans having characteristic structures and substituents are illustrated in Fig. 1. In order to interpret them, the authors[38] analysed the available literature data for the absorption spectra of the SPP themselves and compounds with a structure similar to that of the benzopyran component of the SPP.

It follows from the results of the study of the nature of the electronic transitions in the SPP described above[13,18,25,34,35,37] and from their relation with the photochromic transformations of the SPP[12,22,25] that the long-wavelength absorption band in the spectra of the SPP with an electron-accepting substituent in the benzopyran component is associated with the electronic π–π^* transition localised mainly in the benzopyran

component. The nature of the electronic transitions in the SPP can be analysed on the basis of the fact that molecules with a structure similar to that of the benzopyran component of the SPP belong to the $(\sigma\pi nl)$-type according to the orbital classification of the electronic states of organic molecules with heteroatoms[16]. In such molecules there is a possibility of electronic transitions of the type $n-\pi^*$, $\pi l-\pi^*$, and $\pi l-\pi^*\pi_n^*$ and of the states S_0, $T_{n\pi^*}$, $S_{n\pi^*}$, $T_{\pi l,\pi^*}$, $S_{\pi l,\pi^*}$, $T_{\pi l,\pi^*\pi_n^*}$, and $S_{\pi l,\pi^*\pi_n^*}$.[16] The $\pi l-\pi^*$ and $\pi l-\pi^*\pi_n^*$ transitions represent linear combinations of the one-electron transitions $\pi-\pi^*$, $l-\pi^*$, and $\pi-\pi_n^*$; in the last two transitions the electron of the l orbital of the oxygen heteroatom passes to the π^* orbital of the π system and the π electron of the π system passes to the π_n^* orbital of the electron-accepting substituent. The excitation of the $\pi l-\pi^*$ and $\pi l-\pi^*\pi_n^*$ transitions therefore leads to charge transfer from the oxygen heteroatom to the benzene ring or from the benzopyran ring to the electron-accepting substituent. Thus the $\pi l-\pi^*$ and $\pi l-\pi^*\pi_n^*$ transitions can be characterised as transitions with intramolecular charge transfer (ICT).[16]

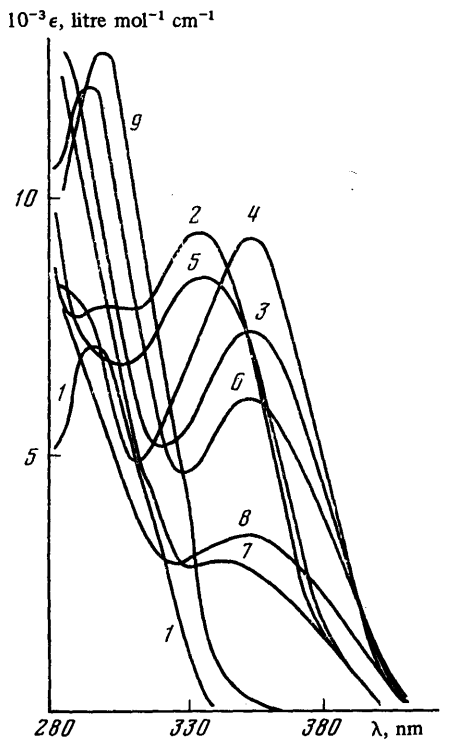


Figure 1. The absorption spectra of the initial forms of spiropyrans in solution in ethyl acetate: 1) SP_1; 2) SP_3; 3) SP_6; 4) SP_8; 5) SP_{11}; 6) SP_{17}; 7) SP_{18}; 8) SP_{20}; 9) SP_{23}.

By virtue of their specific features, the $\pi l-\pi^*$ and $\pi l-\pi^*\pi_n^*$ transitions are apparently closely related to processes which result in the dissociation of the $C_{(2)}-O$ bond; consequently, these transitions can be classified as photochemically active. In the SPP without an electron-accepting substituent in the benzopyran component the $\pi l-\pi^*$ transition must be regarded as a PCA transition. The $\pi l-\pi^*$ transition in 6'-bromo-SP_1 has been designated[22] as $n-\pi^*$ (–O–). It is believed[20] that two transitions are localised in the benzopyran component of SP_1: $n-\pi^*$ and $\pi-\pi^*$ and that the $n-\pi^*$ transition is due to electron transfer from the oxygen heteroatom to the π system of the benzene ring.

On the other hand, if there is an electron-accepting substituent in the benzopyran component of the SPP, then the PCA transition is mainly of the $\pi l-\pi^*\pi_n^*$ type. The corresponding absorption band should have an intensity comparable to that of the $\pi-\pi^*$ transition band and should be located in the long-wavelength part of the absorption spectrum of the initial form of the SPP. In the absorption spectra of the SPP with a nitro-group, this band can be readily identified by comparing such spectra with the absorption spectrum of SP_1 (Fig. 1).

An important characteristic of the PCA transition is the positive charge of the oxygen heteroatom arising on excitation of this transition. It can be determined from the dipole moments of the excited and ground states of the molecule.

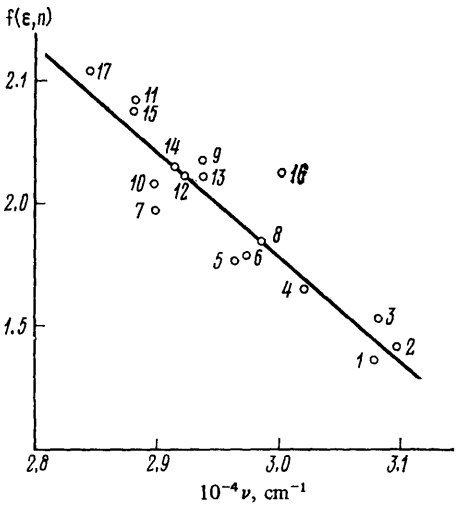
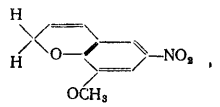


Figure 2. Dependence of the position of the long-wavelength absorption maximum of the initial form of 1,3,3-trimethyl-6'-nitrospiro[indolino-2,2'-(2'*H*-1-benzopyran)] on the universal interaction function $f(\varepsilon,n)$; solvent: 1) hexane; 2) heptane; 3) cyclohexane; 4) carbon tetrachloride; 5) benzene; 6) toluene; 7) chloroform; 8) ethyl acetate; 9) acetone; 10) dichloroethane; 11) pyridine; 12) ethyl methyl ketone; 13) dibutyl phthalate; 14) acetonitrile; 15) dimethylformamide; 16) ethanol; 17) dimethyl sulphoxide.

For quantitative estimates of the above quantities, we employed the theory of solvatochromism[40]. Fig. 2 illustrates the dependence of the shift of the ICT band of SP_3 on the universal interaction function $f(\varepsilon,n)$, which is directly related to the macroscopic characteristics of the medium—the dielectric constant ε and the refractive index n. Assuming a parallel orientation of the dipole moments of both states of the molecule, it is possible to determine the dipole moment of the molecule in the excited electronic state (μ_e)[40]

$$\mu_e = \mu_g - Chcr^3/2\mu_g \qquad (6)$$

from the slope of the linear plot of the solvatochromic shift C, the dipole moment of the molecule in the ground state μ_g, and the radius of the Onsager cavity in the solution r. Here h is the Planck constant and c the velocity of light *in vacuo*. The quantity r was assumed equal to the van der Waals radius of the molecule and was determined with the aid of X-ray diffraction data[5] ($r = 0.6$ nm for SP_3). It is known[41] that the quantity μ_g for the compound is 4.02 D. On this basis, we adopted $\mu_g = 4$ D in order to estimate μ_e for the benzopyran component of SP_8. It was found that $C = -2.2 \times 10^3$ cm^{-1}. Having substituted the selected and determined values of r, μ_g, and C in Eqn.(6), we obtain $\mu_e \cong 15$ D.



Thus the change in the dipole moment of the SP_3 molecule ($\Delta\mu$) on excitation of the photochemically active transition is ~11 D. This is in good agreement with the experimental[42] change in the dipole moment of the *p*-nitrophenol molecule in the S_0-S_1 transition, which amounts to 9 D (it is known[22] that nitrophenols constitute a fairly satisfactory model of the benzopyran component of the SPP with a nitro-group). On the basis of the value of $\Delta\mu$ and on the assumption that the dipole moment of the SP_3 molecule in the $S_{\pi l,\pi^*\pi_n^*}$ state arises from the unlike charges located on the oxygen heteroatom and on the nitro-group, it is possible to estimate the positive charge on the oxygen heteroatom. For a distance between the charges of 0.6 nm, the charge is found to be 0.38 e (where e is the electronic charge). This value agrees very well in its turn with the positive charge on the oxygen atom in the excited singlet state for the *t*-butyl ether of *p*-nitrophenol $(CH_3)_3C-O-Ar-NO_2$, which has been determined experimentally[43] and has been found to be 0.4 e.

It follows from the above results that the excitation of the PCA transition in the SPP does indeed lead to decreased electron density at the oxygen heteroatom in the lowest excited singlet state compared with the ground state. Since a structure of the "electron donor–Ar–electron acceptor" type, for which it is known that both the lowest excited singlet and triplet states are π,π^* states with ICT, can be identified in the benzopyran component of the SPP with an electron-accepting substituent, it appears that the $T_{\pi l,\pi^*\pi_n^*}$ state of the SPP with a nitro-group also involves ICT. This is supported by the finding that the lowest triplet state of the SPP is a π,π^* state (see Section III), and also by analogy with *p*-nitroaniline whose lowest triplet state has been shown[44] to be a π,π^* state with ICT.

Thus the low-lying excited singlet and triplet states of the SPP are highly polar states in which the positive charge is located on the oxygen heteroatom. An increase of the positive charge on the oxygen heteroatom leads to the polarisation of the $C_{(2)}-O$ bond and hence to its weakening. The subsequent redistribution of the electronic excitation energy among the vibrational degrees of freedom of the SPP molecule can apparently be inferred from the available data[16] concerning the mechanism of the distribution of the vibronic excitation energy in heteroatomic organic molecules.

In the study of the vibronic spectra of polyatomic organic molecules the phenomenon of the localisation of the vibronic excitation energy at specific atomic groups was observed[16]. It consists in the fact that the redistribution of energy among the vibrational degrees of freedom takes place primarily at the site of the so-called active vibrations of the molecule (these are, for example, the vibrations of the >C=O, –O–H, etc. groups). Subsequently, the energy of the active vibrations is redistributed among other vibrational degrees of freedom of the molecules of the test compound and the solvent. The active vibrations in the molecule constitute, in particular, the channels through which the selective photodissociation of the molecule takes place[16]. In the case of the SPP the active vibrations are apparently those involving the oxygen heteroatom. This hypothesis is consistent with the finding that the excitation of, for example, antisymmetric –C–O–C– vibrations leads to a higher probability of the dissociation of the $C_{(2)}-O$ bond in the excitation of any other vibrations of the SPP molecule in the excited state[13].

Thus, the mechanism of the dissociation of the $C_{(2)}-O$ bond can be represented as follows[38]: as a result of the excitation of the photochemically active transitions, localised mainly in the benzopyran component, a redistribution of electron density takes place in the SPP, which entails some increase in the positive charge on the oxygen heteroatom and the $C_{(2)}-O$ bond is polarised; in the subsequent redistribution of the electronic excitation energy among the vibrational degrees of freedom (preferentially with respect to active vibrations) the $C_{(2)}-O$ bond is ruptured. This mechanism of the dissociation of the $C_{(2)}-O$ bond can operate not only for spiropyrans but also for chromenes, which are known[13,45,46] to exhibit photochromism.

As mentioned in the introduction, the dissociation of the $C_{(2)}-O$ bond leads to the formation of an unstable configuration of the SPP molecule, i.e. the so-called X-isomer, which in the case of the SPP with an electron-accepting substituent in the benzopyran component and SP_2 has been detected by nanosecond laser photolysis at room temperature[9,10] or by low-temperature spectrophotometry[8–12]. Since the molecule in the states corresponding to the X-isomer can either return to its initial (closed) state or can give rise to the relatively stable coloured form of the SPP, it follows that ϕ_{AB} for the SPP are in the general case not greater than the quantum yield of the $C_{(2)}-O$ bond dissociation reaction [see Scheme (2)], The efficiency of the conversion of the X-isomer into the coloured form B apparently depends, like the efficiency of the dissociation of the $C_{(2)}-O$ bond, on the type and degree of the redistribution of electron density on excitation of the electronic transition in the benzopyran component of the SPP.

V. DEPENDENCE OF THE QUANTUM YIELD OF THE REACTION INVOLVING THE PHOTOCOLOURING OF SPIROPYRANS ON THEIR STRUCTURE

The ideas concerning the nature of the PCA transition, developed by two of the present authors[38,39], make it possible to explain the dependence of the efficiency of the dissociation reaction of the $C_{(2)}-O$ bond in spiropyrans on their structure. As shown in the previous Section, the PCA transition in the SPP involves intramolecular charge transfer and the corresponding absorption band can be characterised as the charge transfer band (CTB) involving charge transfer from the oxygen heteroatom to the benzopyran ring. It is known[40] that the dipole moments of transitions with ICT ($|\mathbf{D}|$) are correlated with the changes in the molecular dipole moment in the transition, i.e. the following relation holds[40]:

$$|\mathbf{D}| \sim |\Delta\mu|. \qquad (7)$$

Since the quantity $|\mathbf{D}|$ characterises the probability of the electronic transition and can be determined from the intensity of the absorption band corresponding to the given transition, it follows that, by virtue of Eqns.(7), it is possible to compare the intensity of the long-wavelength absorption band of the initial form of the SPP with the positive charge on the oxygen heteroatom and hence with the efficiency of the SPP photocolouring reaction.

In order to discover the relation between the intensity of the long-wavelength absorption band of the initial form of the SPP and their structure, one may resort to the available data for the dependence of the CTB intensity on the structure of aromatic compounds with electron-accepting substituents.

1. The addition of an electron-accepting substituent (NO_2, CHO, etc.) to an aromatic system leads to the appearance of an absorption band corresponding to charge transfer from the aromatic ring or from an electron-donating group conjugated with it to an electron-accepting substituent[16,47].

2. The CTB in the spectra of aromatic compounds with a nitro-group correspond to a transition which is polarised along the $C-N_{nitro}$ bond[47,48].

3. The intensity of the CTB depends on the degree of conjugation of the electron orbitals of the electron-donating and electron-accepting groups with the π system of the aromatic rings[16]. The degree of conjugation of the nitro-group with the π system of the aromatic rings can vary as a function of the steric and electronic (mesomeric and inductive) effects of other substituents[40,47,49]; the angle θ between the plane of the nitro-group and that of the aromatic rings can vary correspondingly[47,49].

4. The absorption spectra of *o*- and *m*-nitrophenols are similar and differ significantly from the absorption spectrum of *p*-nitrophenol[40,50]—their CTB have undergone a bathochromic shift[50,51].

5. The presence of two electron-donating substituents and one electron-accepting substituent or of one electron-donating substituent and two electron-accepting substituents in a polysubstituted benzene leads to the appearance in the absorption spectrum of a CTB which represents a superposition of the CTB of the two electron-donating groups so that of the one electron-accepting substituent or of the CTB of the single electron-donating substituent on that of the two-electron-accepting substituents[50,52].

Using the data presented, we shall attempt to explain the variation of ϕ_{AB} for the SPP (see Table) as a function of the wavelength of the exciting light and the SPP structure. In the first place one should note that in weakly polar and non-polar solvents the quantity ϕ_{AB} reaches a maximum value following irradiation of nitro-substituted SPP by light at wavelengths of 365 and 405 nm, which excite mainly the $\pi l-\pi^*\pi_n^*$ transition ($\phi_{AB}^{405}=0.45$ for SP_8 in ethyl acetate at 293 K[38]). The values of ϕ_{AB}^{313} are lower than the corresponding ϕ_{AB}^{365} (see Table). The lower value of ϕ_{AB}^{313} compared with ϕ_{AB}^{365} can apparently be caused by the fact that the light with $\lambda=313$ nm excites the $\pi-\pi^*$ transition in the indoline component of the SPP in addition to the $\pi l-\pi^*\pi_n^*$ transition. On the other hand, the excitation of the indoline component of the SPP can lead to the dissipation of energy through the conformational vibrations of the indoline component[22] and hence to a decrease of ϕ_{AB} for the SPP. Furthermore, the lower value of ϕ_{AB}^{313} for nitro-substituted SPP compared with ϕ_{AB}^{365} can be explained by the fact that the light with $\lambda=313$ nm begins to excite in the benzopyran component of the SPP a transition with an energy greater than that of the PCA transition. The $C_{(2)}-O$ bond dissociation will occur at vibrational levels lying above the electronically excited states. This is indicated, for example, by the strong competition of the photochemical processes with internal conversion to the S_2 states of chromenes and SP_2,[13] as well as the formation of coloured forms of SP_3[9,22] and 6′-methoxy-SP_1[9] under the influence of light at wavelengths of 254 nm[22] and 265 nm[9-22]—this light can excite the S_0-S_3 transition in the benzopyran component of the SPP[25]. However, the excitation of these transitions, which are not photochemically active, does not apparently entail a redistribution of the electron density in the molecule necessary for the stabilisation of form B, and the efficiency of the formation of the coloured form of the SPP from the S_2 and S_3 states is therefore lower than the efficiency of their formation from the S_1 PCA state. This can explain the lower value of ϕ_{AB}^{265} compared with ϕ_{AB}^{365} for SP_3 in petroleum ether[22]. However, unambiguous conclusions are difficult to arrive at, because, as stated in Section I, the indoline fragment of the molecule absorbs in this region, which complicates the interpretation of the results.

As regards SP_2, the PCA transition in the naphthopyran component can only be the $\pi l-\pi^*$ ($2p_z-\pi^*$)[15] transition and its relative contribution to the excitation of the naphthopyran component is smaller than the contribution of the corresponding transition to the excitation of the benzopyran component in view of the more extensive π system in the former case[16]. Light at wavelengths of 313 and 365 nm therefore excites mainly the $\pi-\pi^*$ transitions in the naphthopyran component[13]. These causes also apparently account for the decrease of the values of ϕ_{AB}^{313} and ϕ_{AB}^{365} for SP_2 compared with the corresponding values for the nitro-substituted SPP and ϕ_{AB}^{313} for SP_1 (see Table).

Since the intensity of the $n-\pi^*$ transitions is lower by ~1–2 orders of magnitude than the intensity of the $\pi-\pi^*$ transitions[36], the influence of the $n-\pi^*$ transitions on ϕ_{AB} can be appreciable only in the "tail" of the band corresponding to the PCA transition. Probably for this reason the quantity ϕ_{AB}^{365} for SP_{23} is significantly smaller than ϕ_{AB}^{313}. Indeed the frequency of the $n-\pi^*$ transition, due to the CHO group, is independent of the size of the aromatic π system and amounts to 27000 cm^{-1} (370 nm)[53] and the extinction coefficient at the maximum of the band due to the $n-\pi^*$ transition is 50–60 litre $mole^{-1}$ cm^{-1} for benzaldehyde[47], i.e. amounts to half the extinction coefficient for SP_{23} at 365 nm. On the other hand, light with $\lambda=313$ nm excites mainly the PCA transition in SP_{23} and the value of ϕ_{AB}^{313} for SP_{23} is therefore comparable to ϕ_{AB}^{313} for the SPP of the type of SP_3 (see Table) and Fig.1.

Thus, in relation to the SPP of different structures, it is seen that the successful formation of the coloured form of the SPP under the influence of light requires the excitation of a PCA transition of the type of $\pi l-\pi^*\pi_n^*$.

The variation of ϕ_{AB}^{365} over the series of nitro-substituted SPP can be accounted for by employing the known relations governing the variation of the intensity of CTB in the spectra of aromatic compounds with their structures, which are also presented at the beginning of this Section. Taking these data into account, we shall divide all the nitro-substituted SPP without condensed rings in the indoline part of the molecule into two groups. The first group includes the SPP in the benzopyran component of which it is possible to distinguish a structure corresponding to a substituted *p*-nitrophenol (see Table, SP_3-SP_{16}). The second group includes the SPP whose benzopyran components can be modelled by substituted *m*- and *o*-nitrophenols ($SP_{17}-SP_{20}$). According to the data presented above, the greatest intensity of the band dissociated with charge transfer from the oxygen heteroatom to the nitro-group will occur in the spectra of the SPP of the first group; this is confirmed by the absorption spectra illustrated in Fig.1. Accordingly, the quantity ϕ_{AB}^{365} for this group of compounds is greater than the corresponding quantum yield for the second group.

The variation of ϕ_{AB}^{365} within the groups can also be explained on the basis of the considerations described above. For example, the introduction of the OCH_3 group in the 8′-position (SP_8, SP_9) should reduce the probability of the ICT from the oxygen heteroatom to the nitro-group and hence to a decrease of ϕ_{AB}^{365} compared with ϕ_{AB}^{365} for SP_3, because there is a possibility of a competing charge transfer from the electron-donating OCH_3 group to the nitro-group. Apart from this factor, which leads to a decrease of ϕ_{AB}^{365}, when the OCH_3 or OC_3H_7 group is introduced into the 7′-position (SP_5, SP_6, and SP_7), the steric effect of the substituents will be manifested, leading to the rotation of the nitro-group relative to the plane of the benzene ring and hence to a decrease of the intensity of the PCA transition and the associated band, i.e. to an additional decrease of ϕ_{AB}^{365} (see Fig.1 and Table).

The introduction into the 8′-position of substituents with a weak electronic effect should not influence appreciably the CTB. The insignificant difference between the CTB for SP_{11} and SP_3 (Fig.1) as well as the insignificant decrease of ϕ_{AB}^{365} for SP_{11}, SP_{12}, and SP_{13} compared with ϕ_{AB}^{365} for SP_3 (see Table) are consistent with this. The appreciable decrease of ϕ_{AB}^{365} for SP_{14} following the introduction of a bromine atom in the 8′-position compared with ϕ_{AB}^{365} for SP_3 is apparently caused by the influence of the heavy bromine atom.

The presence of the heavy atom is known[54,55] to be capable of influencing the efficiency of both the intercombination transition and of the non-radiative deactivation of the triplet states of the molecule. The bathochromic shift of the long-wavelength CTB after the introduction in the 7′- or 8′-position of substituents with an appreciable electronic effect is consistent with the available data (see above).

The decrease of ϕ_{AB}^{365} for SP_{20} by a factor greater than 2 compared with that for SP_{18} in conjunction with the small difference between the intensities of the CTB in the spectra of these spiropyrans (Fig.1) may be associated with the fact that in the case of SP_{20} the band associated with the charge transfer from the oxygen heteroatom to the nitro-group is overlapped by the band associated with the charge transfer from the chlorine atom to the nitro-group.

According to X-ray diffraction data for the SP_{18} single crystal[5], the angle θ (see above) in this SPP is 54°. Since the extinction coefficient at the maximum of the band due to the charge transfer from the aromatic rings to the nitro-group is proportional to $\cos^2\theta$,[47,49] it follows that the angle θ for SP_3 can be estimated from θ for SP_{18} and the extinction coefficients at the CTB maxima for SP_3 and SP_{18}. The estimate yields a value of θ close to zero. This result is consistent with the available data for the influence of various substituents in nitrobenzene[47,49] on θ. In particular, in the absence of substituents the angle θ in nitrobenzene is zero and the band associated with the charge transfer from the benzene ring to the nitro-group has its maximum intensity[47,49]. The decrease of ϕ_{AB}^{365} for SP_{16} in dioxan almost by a factor of two compared with ϕ_{AB}^{365} for SP_8 is apparently caused by the mutual steric influence of the nitro-groups in the 5′- and 6′-positions.

The decrease of the values of ϕ_{AB}^{365} for SP_{21} and SP_{22} by more than an order of magnitude compared with ϕ_{AB}^{365} for SP_3 is probably caused by the fact that, when the benzene ring is condensed with the indoline component, the energy levels of the latter are lowered so much that, firstly, this component begins to absorb light with $\lambda = 365$ nm (i.e. the situation observed on irradiation of SPP of the type of SP_3 with light at $\lambda = 313$ nm obtains) and, secondly, the deactivation of the excited states of the benzopyran component by energy transfer to the indoline component becomes possible.

Thus the satisfactory correlation between the ϕ_{AB} for the SPP and the intensity of the long-wavelength absorption band in their spectra as a function of their structure indicates the validity of the identification[38,39] of the long-wavelength absorption band of the initial form of the SPP with the CTB band due to a PCA transition of the type of $\pi l - \pi^*\pi_n^*$ and the validity of the mechanism of the SPP photocolouring reaction based on this finding.

VI. THE MECHANISM OF THE RADIATION-INDUCED COLOURING OF SPIROPYRANS

The first studies on the radiolysis of spiropyrans in frozen solutions were carried out by Hirshberg[56,57], who established that the coloured form of the SPP produced on irradiation with fast electrons is identical with form B, which arises when the SPP is irradiated with ultraviolet light[56]. Further studies of the radiolysis of the SPP in polymers [in polystyrene, poly(methyl methacrylate), polyvinylcarbazole[22,29,39,58]] and benzene solution[7,59,60] showed that the colouring of the SPP on radiolysis takes place mainly as a result of electronic energy transfer from the matrix to the SPP via a triplet–triplet mechanism.

This result permits the conclusion that the colouring of the SPP on radiolysis proceeds mainly via the chemically active triplet state which has been shown in Section IV to be the $T_{\pi l,\,\pi^*\pi_n^*}$ state. Thus the intramolecular dissociation of the $C_{(2)}$–O bond and the formation of the coloured form of the SPP on radiolysis should in essence be of the same type as in the photoexcitation of the SPP and its efficiency should therefore be greater the more effective the population of the chemically active SPP state. This hypothesis is supported by the finding that the variation of the radiation yield of the coloured forms of the SPP (G_B) under the influence of γ-rays at 77 K proved to be similar to the analogous variation of ϕ_{AB} for the SPP (see Table). Consequently, the dependence of the efficiency of the radiation-induced colouring of the SPP on their structure can apparently be explained in terms of the ideas developed in Sections IV and V.

Indeed, it follows from a comparison of the absorption spectra of the initial forms of the SPP in polystyrene (Fig.3) that there is a correlation between the intensity of the CTB and the radiation yield of form B of spiropyrans analogous to the correlation between the intensity of the CTB in the spectrum of a solution in ethyl acetate and the radiation yield of the photocolouring process (G_B).

The influence of substituents on the efficiency of the population of the chemically active triplet state of the SPP on radiolysis can be traced in relation to SP_8. As stated in Section V, apart from the chemically active transition with charge transfer from the oxygen heteroatom to the nitro-group ($\pi l - \pi^*\pi_n^*$ transition), in this SPP there is a possibility of an analogous transition with charge transfer from the electron-donating OCH_3 group to the nitro-group ($\pi l' - \pi^*\pi_n^*$ transition), associated with a band which should undergo a bathochromic shift relative to that of the $\pi l - \pi^*\pi_n^*$ transition. The absorption spectra of the SPP presented in Fig.1 shows that the shift can be by ~2000 cm^{-1}. Since the $\pi l - \pi^*\pi_n^*$ and $\pi l' - \pi^*\pi_n^*$ transitions are of the same electronic type, presumably the $S_1 - T_0$ splittings for these transitions are likewise similar[15,16,36]. Then the sequence of the lowest electronic levels for SP_8 is as follows: S_0, $T_{\pi l',\,\pi^*\pi_n^*}$, $T_{\pi l,\,\pi^*\pi_n^*}$, etc. This sequence of triplet levels leads to an effective

deactivation of the chemically active $T_{\pi l,\,\pi^*\pi_n^*}$ level and hence to an appreciable decrease of G_B for SP_8 compared with G_B for SP_3. Indeed our estimates of the radiation yields of forms B showed that G_B for SP_8 is almost an order of magnitude smaller than for SP_3 (see Table).

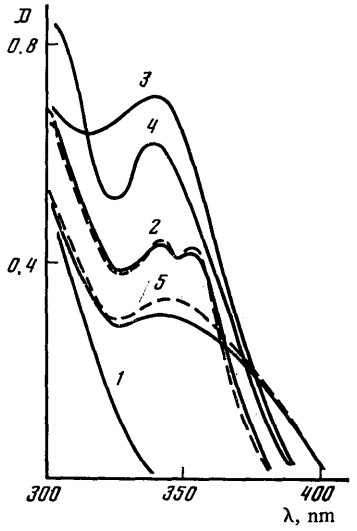
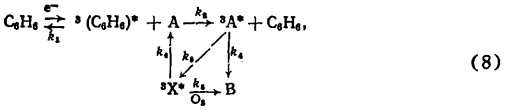


Figure 3. Absorption spectra of polystyrene films of identical thickness with added spiropyrans at equal concentrations at room temperature (continuous lines) and at 77 K (dashed lines): 1) SP_1; 2) SP_2; 3) SP_3; 4) SP_4; 5) SP_{18}.

Analogous results for the dependence of the efficiency of the radiation-induced colouring of the SPP on their structure were obtained in a study of the pulse radiolysis of benzene solutions of indoline SPP (compounds SP_3^*, SP_8^*, and SP_{14}^*), having benzopyran components similar to those of SP_3, SP_8, and SP_{14} respectively[7,58,59,60]. Kryukov and Vannikov[60] published a mechanism of the colouring of the SPP on radiolysis:

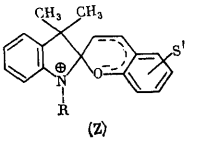


where $^3X^*$ is the triplet state of the X-isomer of the SPP. The rate constants for the formation of form B in a solution through which helium is bubbled have the following values (s^{-1}): $k_4 \geq 10^8$ and $k_8 \cong 10^4$, while in the presence of oxygen we have $k_4 \geq 10^8$ and $k_8 \cong 1.5 \times 10^6$.[59,60] It has been noted[59,60] that the ratio of the rapid and slow stages in the formation of form B depends greatly on the SPP structure. For example, the ratio of the optical densities of form B at the maximum of its long-wavelength absorption band $D^1_{\lambda max}/D^2_{\lambda max}$ ($D^1_{\lambda max}$ was measured immediately after a 40 ns pulse and $D^2_{\lambda max}$ was measured after 1 μs) is 0.6 for SP_3^*, 0.3 for SP_{14}^*, and 0 for SP_8.[60] The absence of a rapid stage in the reaction involving the formation of form B for SP_8 can be explained by the fact that the chemically active $T_{\pi l,\,\pi^*\pi_n^*}$ ($^3A^*$) state is effectively deactivated as a consequence of the internal transition to the $T_{\pi l',\,\pi^*\pi_n^*}$ state, which is chemically inactive.

It has been noted[60] that the method of pulse radiolysis is preferable for the investigation of the mechanism of the formation of the coloured form of the SPP from the triplet states of the initial form of the SPP compared with the method of sensitised photocolouring of the SPP in view of the fact that the introduction of high concentrations of triplet energy donors introduces an uncertainty into the interpretation of the processes occurring in the system.

A short-lived absorption band in the region of 450 nm has been discovered[59] and assigned to the triplet–triplet transition of the intermediate, which is a *cis*-cisoid isomer of the SPP (X-isomer) in the triplet state. At the same time the ground state of the X-isomer was not manifested optically in the wavelength range from 450 to 650 nm[59] (the absorption band due to the S_0–S_1 transition of the X-isomer is in the range 440–460 nm[6,9–11]).

The establishment of the triplet states of the initial forms of the SPP in the photolysis of single crystals of nitro-substituted SPP at low temperatures has been observed[61,62] by EPR. The author[61] attributed the observed EPR signals to the EPR spectrum of a radical pair with an average distance between the paramagnetic centres of 0.26 nm. It has been suggested[29,61] that the radical pairs are formed as a result of an intramolecular electron phototransfer from the indoline component of the SPP to its benzopyran component and can be represented schematically as follows:



(Z) (9)

The distance between the nitrogen and oxygen heteroatoms of the indoline and benzopyran components, determined by X-ray diffraction[5], is 2.3 Å. Bearing in mind that the difference between this quantity and the average distance between the paramagnetic centres in a triplet radical pair can be due to the steric delocalisation of the interacting electrons and the inaccuracy of the description of their interaction by the point dipole moment[63], it appears that the mechanism of the formation of these pairs proposed by the present authors[29] does indeed operate. It is noteworthy that it has also been suggested[15,29] that the intermediate Z is involved in the photocolouring of the SPP. We may point out that generally speaking the triplet state of the X-isomer, to the triplet–triplet absorption of which a short-lived band at 450 nm has been ascribed[59,60], may be similar to Z in its nature.

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Aspartame and Its Analogues

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The results of studies on the biochemistry of the sweet taste are briefly reviewed. The methods of synthesis of "aspartame"—a sweet dipeptide—are considered, its structural analogues are described, and quantitative estimates are made of the degree of sweetness relative to sucrose. Attention is concentrated mainly on problems of the relation between the structure of the substance and its taste in the series of aspartyl derivatives.
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I. INTRODUCTION

After the accidental discovery by Schlatter and coworkers[1] in 1969 of the sweet taste of the methyl ester of α-L-aspartyl-L-phenylalanine, numerous studies devoted to the synthesis and applications of "aspartame" (this was the name given to this sweet preparation, first manufactured on an industrial scale by the American G.D.Searle Company[2]) have been published. The study of the structural analogues of aspartame from the standpoint of their taste merits no less attention. Studies on these lines have been prosecuted on a wide scale since 1969 until today and have made a considerable contribution to the theory of the sweet taste. The problem of the relation between structure and taste, the solution of which will permit a specific search for new intensely sweet compounds, its particularly urgent[3].

The increased interest in sweet peptides is justified also from the practical point of view. The need for synthetic flavours designed to replace sucrose continuously increases[4,5]. Many representatives of the series of dipeptide esters are superior to sucrose as regards the intensity of the taste by factors of hundreds and thousands. Their application would make it possible to reduce sharply the calorie content in view of the small amount of substance required. The assimilation of such products is unrelated to insulin. By virtue of these properties, sweet peptides (together with other low-calorie natural and synthetic sweet substances) can be used in low calorie diets and are recommended primarily for patients suffering from obesity and sugar diabetes[4-9].

Being indifferent to microorganisms, sweet dipeptides such as aspartame are particularly convenient for pharmaceutical use (for example for the sweetening of medicines, which is extremely important for the treatment of children[10-12], particularly since aspartame is safe for both children and adults[13]). From the medical point of view, aspartame has yet another important advantage over sucrose: it does not stimulate the development of dental caries[5].

When aspartame is used in combination with sucrose, glucose, cyclamate, or saccharin, a synergistic effect is produced, as a result of which the consumption coefficients of both mixture components are reduced[5]. Furthermore, it has been observed that the addition of a small amount (2–3 wt.%) of aspartame or some of its analogues to saccharin fully masks its unpleasant flavour[12].

Among the most widely used synthetic sweeteners employed abroad at the present time (particularly in the USA), aspartame is superior as regards its taste[4,5]. The metabolism and potential toxicity of aspartame have been thoroughly investigated[14,15]. This preparation has withstood numerous tests for toxicity and carcinogenic properties and is contraindicated only for patients suffering from phenylketonuria[2,5]. It has been noted that aspartame influences the pH of human whole saliva and tends to alter the concentration of lactic acid in it[16].

Aspartame is convenient for use in a wide variety of dietary compositions[5]. The only limitation is its lability with respect to hydrolysis in strongly acidic and neutral-alkaline media, particularly on heat treatment[5,17]. Methods have been proposed for the modification of labile dipeptide esters which eliminate this disadvantage. One of the ways of reducing the hydrolytic lability of sweetening agents consists in binding the molecules responsible for the sweet taste to macromolecules, for example, dextran[18,19] or the soya-bean protein extract[20]. Such molecular aggregates are obtained when aqueous solutions of both components are dried together (in the required proportions) by spraying or sublimation. It is then important to find the optimum size of the aggregate, since an increase of molecular size hinders the attainment of the required contact with the receptor and can lead to an appreciable decrease of the degree of sweetness. Another way is to synthesise compounds with a structure similar to that of aspartame but without a tendency towards hydrolysis and the formation of diozopiperazine derivatives in aqueous solutions[21]. (These compounds are considered in Section 4 of the present review.)

Thus the importance of synthetic peptide flavours is evident. The problem arises of the development of the most rational and economical syntheses of the best examples of the compounds under consideration, which would make them sufficiently readily available at least for therapeutic purposes.

II. CERTAIN ASPECTS OF THE BIOCHEMISTRY OF THE SWEET TASTE

Before considering the methods of synthesis and the structure–taste relations for the enormous number of compounds obtained on the basis of the aminoacids, it is useful to describe briefly the problems of the theory of the sweet taste.

The taste reaction is a complex phenomenon which has been inadequately investigated. The perception of taste arises as a result of the interaction of the molecules of the substance stimulating the taste (tastant) with the corresponding chemoreceptor. The human sensor systems incorporate several types of the so-called taste buds, i.e. sensitive sections of the tongue. It has been established[22] that the receptors responsible for the sweet taste are located

mainly in the front part of the tongue in mushroom-shaped buds. The buds contain taste cells, in the membranes of which chemoreceptors are believed to be distributed[23,24].

The protein forming complexes with sugars and apparently behaving as a receptor responding only to sweet substances[25–29] has been isolated from the epithelial tissues of animal tongues and was subsequently investigated. The primary chemoreception processes were investigated at the molecular level for the first time by Beidler[30–32], who established, in particular, that physical processes of the type of adsorption underlie the interaction of the tastant with the active centres of the plasmatic membrane of the tast cell, this hypothesis was subsequently confirmed[33].

The wide variety of sweet substances having completely different compositions, constitutions, and geometric structures interfered for a long time with the discovery of the principal distinctive features common to all sweet compounds and enabling the receptor to recognise them. A specific common feature of sweet molecules was discovered by Shallenberger and Acree[34], who specified the concept of contact between the tastant and the receptor, having established that such contact is achieved via hydrogen bonds formed within specific sections of the molecule of the tastant and the active centres of the receptor. They claim[34] that a sweet substance must have two polar functional groups, one of which behaves as a proton donor and the other as a proton acceptor; they designated them by AH and B. In order to achieve two-point binding of the molecule to the receptor via hydrogen bonds, the distance between the atoms or groups of atoms A and B in the molecule must correspond to the distance between the active centres of the receptor. It has been established[34] that it amounts to ~3 Å.

Although this theory is in fact imperfect, it is nevertheless valid in relation to different classes of compounds with a sweet taste. The mechanism of the interaction of the receptor–sweetener pair was refined on the basis of data obtained in the study of the taste of aminoacid stereoisomers[35–39]. The fact that many D-aminoacids are sweet, while their L-isomers are tasteless or bitter indicates the stereospecificity of the chemoreceptor and leads to the conclusion that there exists a third contact between the tastant and the receptor. By calculating the interaction energy in the tastant–receptor model system, it was shown[40] that this type of interaction represents hydrophobic binding. Consequently, apart from the AHB polar system, the tastant molecule should contain a hydrophobic region (it will be designated by X) oriented appropriately[41].

The degree of hydrophobic binding to the receptor apparently determines the intensity of the taste. Deutsch and Hansch[42] and Holthae and Kier[41] demonstrated the existence of this correlation in relation to alkyl-substituted 2-amino-4-nitrobenzenes. It will be shown below, in relation to specific examples, how great is the influence of the hydrophobic properties and the geometric form of the substituents in the side chain in the series of aspartame analogues on the intensity of the taste of these compounds. It has been suggested that the third binding region X in the series of dipeptide esters is located at the centre of a branched substituent in the side chain; for example, this is the centre of the benzene ring in the case of aspartame[43].

It has been suggested[44–46] that the more exact the correspondence of the surface features of the tastant molecule and the "working" surface of the receptor, the more readily is the required contact between them attained and the stronger the perception of the taste. The external form of the "sweet unit" can thus serve approximately as a model of the active receptor surface[46]. One of the preferred conformers of aspartame, which is capable of binding to the receptor without steric hindrance, was chosen as a model[44–46] (Fig. 1a). The authors claim that this model surface of the receptor is consistent with the shape of the molecules of sweet substances of different types, which can be useful for the prediction of the taste of new structural analogues of aspartame and other compounds.

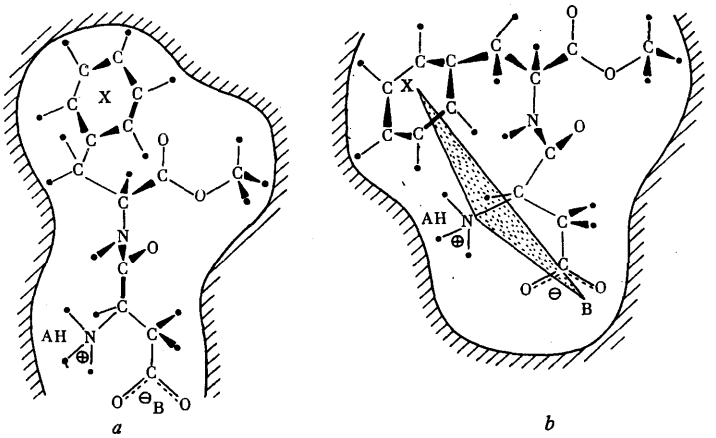


Figure 1. The suggested conformation of the aspartame molecule and of the active site of the taste receptor according to the data of Lelj et al.[44] (a) and Heijden et al.[43] (b).

Another aspartame conformer was selected as a model of the receptor by Heijden et al.[43] (Fig. 1b). According to the authors[43], only for this structure of the sweet dipeptide can the identity of the taste be influenced by the dimensions and geometrical shape of the side chain and of the terminal ester group, which ensure the maximum coupling with the receptor when the correspondence between the surfaces is satisfactory; furthermore, the structural data for this conformer agree best with the calculated A–B–X distances. Yet another model of the hydrophobically binding part of the receptor, obtained on the basis of structural data for the sweetest diesters of α-aspartylaminomalonic acid, has been proposed[47]. The contradictions between different authors as regards the topology of the taste receptor are due to the fact that their conclusions are based on calculations for individual static conformations of aspartame (or other sweet compounds) without taking into account the structural changes in the course of the interaction with the receptor. More accurate data can be obtained by the direct investigation of receptor–dipeptide ester complexes.

Despite the available data[24,40,48–53], the mechanism of the interaction of the tastant with the receptor required further thorough investigation. One cannot rule out the possibility that certain enzymes are involved in the perception of taste[24,54].

III. METHODS OF SYNTHESIS OF ASPARTAME

The methyl ester of α-L-aspartyl-L-phenylalanine has an intense sweet taste, being 150–180 times sweeter than sucrose. One of its component aminoacids (phenylalanine) is an unsubstituted natural aminoacid.

Numerous studies have been carried out on the methods of synthesis of aspartame. The most attractive procedure in view of its ease and the low cost of the starting material is

the method based on the aminolysis of the inner anhydride of aspartic acid. The anhydride of aspartic acid with the amino-group protected by groups usually employed in peptide synthesis (benzoxycarbonyl, t-butoxycarbonyl, o-nitrophenylsulphenyl, formyl, etc.[55–60]) and the anhydride in the form of different salts[61–66] are used equally widely. The aminolysis is carried out in organic solvents, aqueous organic mixtures, and water (at a specific pH)[59].

The aminolysis of the salts of aspartic acid anhydride can be carried out selectively with the preferential formation of the α-isomer by reducing the temperature, by employing an excess of the amino-component, and by introducing various additives into the reaction mixture[61]. These additives can be (1) acids (acetic acid[61], carbon dioxide[62–64], and orthophosphoric acid[65]); (2) mixtures of weak acids and lower aliphatic alochols[62]; (3) mixtures of strong acids and alcohols[66,67]. Aqueous solutions of inorganic bases have been used for the same purpose as additives in the aminolysis of the *N*-benzoxycarbonylanhydride of aspartic acid[68].

The above group of methods is characterised by general advantages and disadvantages: on the one hand, there is the evident simplicity and low cost of the method of synthesis and, on the other hand, the problem of freeing the main product from undesirable (in the given synthetic scheme) impurities, primarily the corresponding β-isomer, which is difficult to separate from the main product and has bitter taste[69–71].

The problem of separating the α- and β-isomers having opposed tastes is solved in different ways, which are based on the following factors: (1) on the different solubilities of their salts with strong inorganic acids[58,72,73] or with aromatic acids[74] (the α-isomer salts are usually less soluble in aqueous and aqueous organic media than the corresponding salts of the β-isomer); (2) the reduced reactivity of the β-isomer in the reaction with ketones. On treatment with acetone, the α-isomers of aspartame and some of its analogues readily form the corresponding 4-imidazolidinones, which are readily soluble in acetone; the β-isomers, which do not react, remain insoluble[75,76]. The latter method suffers from the following disadvantage: in order to isolate aspartame in a free form, the fairly stable 4-imidazolidinone must be hydrolysed at an elevated temperature, whereupon there is a possibility[77] of the partial decomposition of the labile aspartame.

A novel method has been proposed for synthesising aspartame, which has been recommended as an industrial procedure; it is based on the interaction of the *N*-protected aspartic acid with the amino-component in the form of an ester of an *N*-carbonylaminoacid[78]. The main disadvantage of this method is the necessity to work with phosgene at elevated temperatures (this imposes certain requirements on the apparatus) and also the inevitable formation of the β-isomer as a side product.

Aspartame has been obtained[79] by the interaction of the *N*-protected aspartic acid with formaldehyde and subsequent aminolysis of the oxazolidinone, which, in view of its inadequate reactivity, reacts with the amino-component only at an elevated temperature (50 °C). A method has been developed for the synthesis of sweet α-aspartyl derivatives using the *N*-carboxyanhydride of a β-*O*-protected derivative of aspartic acid[80]. A bottleneck in this procedure is the stage involving the aminolysis of the *N*-carboxyanhydride, which is achieved in the pH range 9–12 and under these conditions there is a possibility of the hydrolysis of the ester group.

Aspartame has also been synthesised[81] by a non-traditional method from the dichloride of maleic acid. It is important to note that this yields only the DL–L-form. It has been suggested that aspartame be obtained from (*S*)–4-vinylazetidin-2-one,[82] but the method is inconvenient owing to the instability of the intermediates.

Naturally the classical methods of peptide synthesis (the carbodi-imide, mixed anhydride, or activated esteer methods) have also been used to obtain aspartame and its analogues[83–85]. Their advantages and disadvantages are well known[86]. A version of the synthesis of aspartame using the convenient condensing agent trifluoroacetoxysuccinimide has been described[87]. This reagent ensures the rapid and complete conversion of the *N*, β-*O*-disubstituted carboxy-component into the corresponding α-*N*-hydroxysuccinimide ester, which readily undergoes aminolysis.

Modified methods for the removal of the protecting groups in the course of the synthesis of free dipeptide esters with a sweet taste have been put forward[88–90]. It has been reported[91] that the manufacture of aspartame by an enzymatic method from racemic aminoacids, which are the most convenient and economical starting material, has been stablished in Japan[91].

Table 1. The relative degrees of sweetness (RS) of aspartame, its isomers, and analogues[1].

Compound	RS*
Sweet	
α-(L)-Asp-(L)-Phe—OMe	100—150
α-(L)-Asp-(L)-Met—OMe	100
α-(L)-Asp-(L)-Tyr—OMe	10
α-(L)-Asp-(L)-Phe—OEt**	10
α-(L)-Asp-(L)-Phe—OPr-n**	1
α-(L)-Asp-(L)-Phe—OPr-iso**	1
α-(L)-Asp-(L)-Phe—OBu-t**	1
Tasteless	
α-(L)-Asp-(L)-Phe	0
α-(L)-Asp-(L)-Phe—NH_2	0
α-(L)-Asp-(L)-Phe (NH₂ on Phe)	0
Bitter	
α-(L)-Asp-(L)-Phe (OMe on Phe)	
β-(L)-Asp—(L)-Phe—OMe	
α-(L)-Asp-(L)-Phe	
β-(L)-Asp—(L)-Phe	
α-(L)-Glu-(L)-Phe—OMe	
α-(L)-Asp-(D)-Phe—OMe	
α-(D)-Asp-(L)-Phe—OMe	
α-(D)-Asp-(D)-Phe—OMe	

*Here and henceforth the degree of sweetness of sucrose was assumed to be unity.

**According to the data in Refs. 55 and 83.

IV. RELATION BETWEEN THE STRUCTURE OF A SUBSTANCE AND ITS TASTE IN THE SERIES OF ASPARTAME ANALOGUES

1. Esters of α-aspartyl-containing Dipeptides

Mazur et al.[1] achieved the synthesis of a large series of aspartame analogues (~50 compounds) and reached the first conclusions concerning the structure—taste relation for aspartyl-containing derivatives. The following requirements must be met for a given substance to have a sweet taste: (1) unsubstituted amino- and carboxy-groups must be

present with a specific distance between them; (2) a specific configuration of the asymmetric carbon atom is necessary; (3) an ester group must be present at the C-end of the dipeptide. The authors[1] assumed that, even if only one of these requirements is infringed, the sweet taste disappears (Table 1). Later it was shown that these conditions are not obligatory for the retention of the sweet taste in the series of aspartyl-containing compounds.

When the α-aspartyl residue was replaced by other aminoacids, even one with a similar structure such as **glutamic** acid, not a single sweet dipeptide was obtained[1]. The explanation is apparently that, for the interaction with the receptor, it is important that that AHB system should be planar, i.e. in the given instance that the amino- and carboxy-groups of the N-terminal aminoacids should form a planar cyclic zwitter-ionic form[44,48] (Fig.2). This condition can be fulfilled only when the *N*-terminal aminoacid is aspartic or aminomalonic acid. As regards the second part of the aspartame molecule, the latter can undergo various changes to a greater extent. For example, phenylalanine can be replaced by L-tyrosine or L-methionine without loss of the sweet taste.

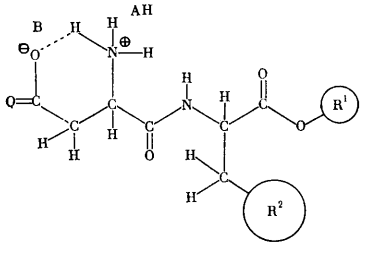
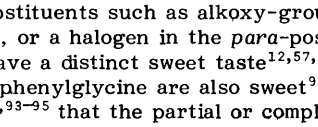


Figure 2. The esters of sweet α-aspartyl-containing dipeptides.

In order to test the requirements imposed on the stereochemistry of the molecule, L–D, D–L-, and D–D-isomers of aspartame were synthesised; they all proved to be bitter. Schlatter[84] showed that the sweet taste does not disappear fully in the DL–DL-, DL–L-, and L–DL-modifications, although the degree of sweetness of these compounds is lower than that of the L–L-isomer.

The data of Mazur et al.[1] demonstrate the influence of the size of the C-terminal ester group on the intensity of the sweet taste, namely the intensity of the sweet taste decreases with increase of the size of the ester group. This shows that variations in the size of the molecule are not unimportant for the taste receptor and confirm the validity of the conclusions of Heijden et al.[43]

Mazur and coworkers[83] extended the list of sweet dipeptides by discovering that these include also the esters of L-α-aspartyl-L-threonine, L-α-aspartyl-*S*-alkyl-L-homocysteine sulphone. The aspartame analogues obtained by introducing substituents such as alkoxy-groups, the hydroxy-group, or a halogen in the *para*-position of the benzene ring have a distinct sweet taste[12,57,83]. The esters of L-α-aspartylphenylglycine are also sweet[92]. It has been observed[10,57,78,93–95] that the partial or complete hydrogenation of the benzene ring in compounds having the general formula

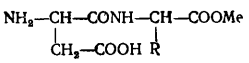


R^1=Alk

R^2=H, OH, OAlk, or Hal

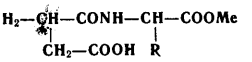
has a favourable effect on the intensity of the sweet taste.

In their study of the contribution of different structural elements to the sweet taste of dipeptide esters, Mazur et al.[95] established that the C-terminal aminoacid can be aliphatic and showed that the intensity of the sweet taste of compounds of the type



varies with the size, form, and hydrophobic properties of the group R [95,96] (Table 2). It was noted that the methyl esters of L–L-dipeptides of this kind do not have a sweet taste as long as the number of carbon atoms in the chain of R does not reach four.

Table 2. The esters of α-aspartyl-containing dipeptides* of the type

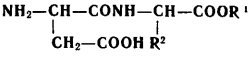


R	RS	Refs.	R	RS	Refs.
Me	0	[95]	n-Pent	50	[95, 96]
iso-Pr	0	[95]	iso-Pent	80	[95, 96]
n-Bu	40	[95, 96]	n-Hex	70	[95, 96]
iso-Bu	0	[95]			

*L–L-configuration.

In the series of α-aspartylalanine and α-aspartyl-*C*-alkylglycine esters, the sweetest dipeptides proved to be those with the L–D-configuration[85,95,97] (Table 3). These compounds are distinguished by the following feature: if the C-terminal ester group R^1 is sufficiently large, as in the case of the n-propyl or isopropyl esters, the group R^2 must be small in order to obtain an intense sweet taste; with increase of its size, the degree of sweetness diminishes[85,95] (Table 3).

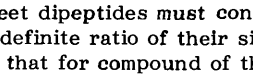
Table 3. The esters of α-aspartylalanine and α-aspartyl-*C*-alkylglycine*:



R^1	R^2	RS	References
Me	Me	25	[95]
Et	Me	80	[95, 97]
n-Pr	Me	170	[85, 95, 97]
iso-Pr	Me	125	[85, 95, 97]
n-Bu	Me	10	[95]
n-Pent	Me	6	[95]
iso-Pr	Et	170	[85, 95, 97]
iso-Pr	iso-Pr	170	[85, 95, 97]
iso-Pr	n-Pr	17	[95]
iso-Pr	s-Bu	4	[95]
iso-Pr	iso-Bu	0	[95]
iso-Pr	n-Bu	0	[95]

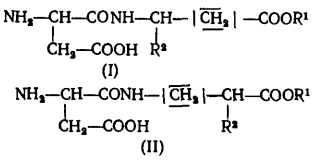
*L–D-configuration.

In general, all sweet dipeptides must contain two hydrophobic groups with definite ratio of their sizes[48] (Fig.2). It has been shown[98] that for compound of the type



there is a possibility (without loss of sweet taste) of certain combinations of the substitutents R^1 and R^2, which can be aliphatic, alicyclic, or aromatic. It has been noted[99] that the salts of such compounds with certain acids, for example, with malic, citric, etc. acids, are particularly sweet. It has also been recommended that aspartame be used in combination with citric acid[100,101]. The intensification of the taste of dipeptide esters in the presence of citric acid had been observed earlier[10]. Presumably in this case Beidler's hypothesis[23] that the conformation of the membrane of the taste cell varies with the pH of the medium, which can intensify the sweet taste in the presence of the tastant, is valid in this case.

In their search for hydrolytically stable aspartyl derivatives, Miyaoshi et al.[21] synthesised compounds of a new type. In order to rule out the possibility of the formation of substituted dioxopiperazine, they introduced an additional methylene group in various positions along the peptide chain and obtained two types of compounds with an L–D-configuration:

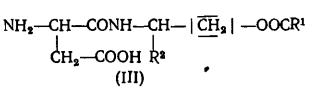


(I)

(II)

Although the length of some of these compounds is similar to that of the n-propyl ester of L-α-aspartyl-D-alanine, the relative sweetness of which amounts to 170 units, the rearrangement of the molecule induced undesirable changes in the structure, which led to a decrease of the level of sweetness to 20 units.

Compounds of type (III), obtained with an increase in chain length, as in compounds (I), with a simultaneous transformation of the terminal carboxy-group, proved more successful:



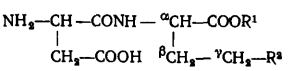
(III)

Eleven *O*-acyl-2-(L-α-aspartylamino)-D-alkanols (III) proved sweeter than sucrose by a factor of 100 and more[21]. The structural requirements which must be met by these compounds as regards the dimensions of the hydrophobic groups R^1 and R^2 are the same as for the dipeptide esters. The configuration of the 2-aminoalkanol esters must correspond to the D-form of the aminoacids; none of the *O*-acyl-2-(α-L-aspartylamino)-L-alkanols proved to be sweet. *N*-(L-α-aspartyl)-*O*-cyclobutyl-D-alaninol is 220 times sweeter than sucrose and, in contrast to aspartame, withstands boiling in aqueous solution at pH 4 and 7 for 1 h without appreciable changes in the taste[21].

The structure–taste relations for α-aspartyl derivatives of hydroxyaminoacids have been investigated[102–104]. The esters of L-α-aspartyl-L-β-(*erythro* and *threo*)-hydroxynorleucine, -*O*-actyl-L-serine, -D-serine, -D-threonine, and -D-allothreonine have been synthesised and their taste compared with that of the corresponding dipeptide esters without a hydroxy-group[103]. It was observed that the introduction of the hydroxy-group has different effects on the taste of the L–L- and L–D-dipeptides: it reduces the sweet taste in the series of L–L-peptide esters and intensifies it in the series of the L–D-isomers. For example, the esters of L-α-aspartyl-D-serine and L-α-aspartyl-D-threonine proved to be sweeter than the corresponding esters of L-α-aspartyl-D-alanine and L-α-aspartyl-D-α-aminobutyric acid. It was also found that the *threo*- and *erythro*-isomers differ in the intensity of the taste[103]. Whereas in the series of the esters of the L–L-dipeptides the sweetest derivatives were the methyl esters[1], among the hydroxy-analogues with the L–D-configuration the n-propyl and isobutyl esters are sweetest[102,103].

The replacement of the methyl group in the side chain in the series of *O*-acyl-*O*-2-α-L-aspartylamino-D-alkanols[21] by the hydroxymethylene group increased the level of sweetness in one case, while in the remaining cases it caused a decrease.

The branching of the side chain by the introduction of even one methyl group in the β- or γ-position resulted in bitter compounds in the series of both hydroxy- and deoxy-derivatives of dipeptide esters[103]:



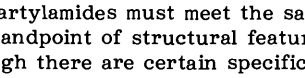
The above data show that the presence of a free or substituted hydroxy-group (depending on its location in the side chain) prevents the hydrophobic binding of the molecule to the receptor only in some cases.

In order to investigate the influence of the nature of the side chain on the intensity of the sweet taste of the esters of aspartyldipeptides, Brussel et al.[104] synthesised a series of structurally similar analogues based on *S*-alkyl-L-cysteine, *O*-alkyl-L-serine, *O*-acyl-L-serine, and asymmetric aminomalonic diesters. The dimensions of the dipeptide side chain were determined on molecular models of these compounds and the characteristics of the shape of the chain were investigated in each specific case. The authors[104] concluded, like Mazur et al.[95], that the intensity of the sweet taste of all the compounds obtained depends on the hydrophobic properties, dimensions, shape, and steric characteristics of the side chain. It has been shown clearly[104] that the degree of branching of the group R^2 in the side chain is not the only important feature, a specific geometrical position of the branching point on the side chain being more significant.

These facts show that the group R^2 of the side chain of the dipeptide ester actually interacts with the hydrophobically binding site of the receptor[43]. This conclusion is valid only in relation to L–L-dipeptides; the hydrophobic binding of the L–D-dipeptides to the receptor is possible only for the C-terminal ester group (because of the different steric dispositions of the substituents at the asymmetric carbon atom of the D-aminoacid), while in *N*-L-α-aspartyl-*O*-acyl-D-aminoalkanols this is possible only for the acyl group. This in fact explains the earlier observation[85,95,97,103] that the degree of sweetness of α-aspartyl derivatives with the L–D-configuration increases with the size of the ester group and with decrease of the bulk of the side chain.

2. α-Aspartylamides

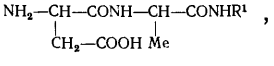
Having synthesised a series of α-aspartylamides, Mazur[105] showed for the first time that the ester group is not an obligatory element in sweet derivatives of aspartic acid; this was later confirmed in relation to aspartylacylaminoalkanols[21], which is not surprising, since the transformations of the terminal carboxy-group in L–L-dipeptides do not involve the main part of the molecule—its glucophore, which is intrinsically involved in the interaction with the receptor. This is why α-aspartylamides must meet the same requirements (from the standpoint of structural features) as dipeptide esters, although there are certain specific differences. To retain the sweet taste, it is necessary that the methyl group be present in the α-position:



Furthermore, when optically active amines are used as the starting materials, steric similarity to L–L-dipeptides must be maintained.

In the series of α-aspartylphenylalkylamides the introduction of a halogen in the *para*-position of the benzene ring as well as hydrogenation of the latter did not intensify the sweet taste[105], as had been observed for dipeptide esters. The aromatic component of aspartylphenylalkylamides can be replaced by an aliphatic chain, as in the case of dipeptide esters. The chain length of the sweetest compounds corresponds to seven carbon atoms; its decrease or increase leads to less sweet or tasteless derivatives. As was to be expected, the form of the chain influences the intensity of the taste. The sweetest α-aspartylamide is α-aspartyl-α,δ-dimethylpentylamide, being 100 times sweeter than sucrose; compounds sweeter than aspartame have not been discovered among them.

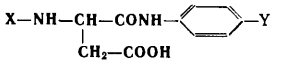
A group of sweet L-α-aspartyl-D-alanylamides of the type



where R^1 = Bu, iso-Bu, s-Bu, or cyclo-Hex, were later synthesised[106]. The level of their sweetness is approximately equal to that of aspartame (they are 100–125 times sweeter than sucrose)[106].

It is of interest to note that the presence of the α-amide linkage in all the known derivatives of aspartic acid is necessary for a sweet taste. If the amide group is alkylated or replaced by an ester group, the taste changes to bitter or disappears respectively; this transformation apparently alters the conformation of the compound so much that a three-point interaction with the receptor becomes impossible[48].

Table 4. N-Acyl-L-α-aspartylanilides:



No.	X	Y	RS	References
1	CF_3CO	H	12	[107—111]
2	CF_3CO	Cl	120	[107, 108, 109, 111]
3	CF_3CO	F	1	[107, 108, 109, 111]
4	CF_3CO	Br	120	[107, 109, 111]
5	CF_3CO	I	*	[107]
6	CF_3CO	CN	3000	[107, 108, 109, 111]
7	CCl_3CO	H	1	[107, 108, 111]
8	CCl_3CO	Cl	**	[108, 111]
9	CCl_3CO	F	**	[108, 111]
10	CCl_3CO	CN	3000	[107, 108, 111]
11	H	CN	12	[107, 111]

*Bitter.

**Sweet product; a quantitative estimate of the RS is not given in the original communications.

3. *N*-Acyl-α-aspartyl Derivatives

The discovery of a sweet taste in certain *N*-acyl derivatives of aspartic acid was quite unexpected[107]. The sweet taste of one of these, namely trifluoroacetyl-L-α-aspartylanalide (No.1 in Table 4), was discovered accidentally[107] (like the taste of aspartame) and could not be explained from the standpoint of the existing ideas concerning the necessity for the presence of a free amino-group in all sweet α-aspartyl derivatives. Not until 1978 was it suggested[46] that the AHB system is mainly required to fix the molecule on the active surface of the receptor. Consequently a single hydrogen bond formed by the carboxy-group may be sufficient to retain the molecule, provided that it is sterically compatible with the receptor surface[46].

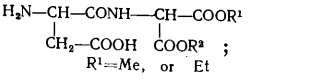
Lapidus and coworkers[107–111] noted the following features characteristic of *N*-acyl-L-α-aspartylanilides (Table 4). The introduction of a single halogen atom (except iodine) or the cyano-group in the *para*-position of the benzene ring of the anilide intensifies the degree of sweetness of the substance. The introduction of a halogen in the *ortho*- and *meta*-positions or the introduction of two halogen atoms does not lead to sweet derivatives. The introduction of substituents such as the methyl, trifluoromethyl, and hydroxy-groups in the *para*-position in the ring also has a negative influence on the taste. Among all the acyl groups tested, only the trifluoroacetyl and trichloroacetyl groups are capable of forming sweet derivatives. These two groups are apparently approximately equivalent as regards their influence on the intensity of the sweet taste (cf. Nos.6 and 10 in Table 4). Comparison of the tastes of individual *N*-acylaspartylanilides (Nos.6 and 10 in Table 4) and their analogues with free amino-groups (No.11 in Table 4) shows that the level of sweetness falls sharply following the removal of acyl groups (from 3000 to 12 units).

As in the series of dipeptide esters, the derivatives of D-aspartic acid lack sweetness entirely[107]. The introduction of the trifluoro- or trichloro-acetyl group into the amino-group of aspartame did not entail either an intensification or a weakening of the taste[107,108,111]. One should note that the synthesis of the *N*-trifluoroacetyl derivatives of aspartame is much simpler than that of aspartame itself; it is achieved in a single stage by the aminolysis of the *N*-trifluoroacetylanhydride of aspartic acid and there is no need to remove protecting groups. Unfortunately, the papers of Lapidus and coworkers[108–111] do not contain information about the methyl ester of *N*-trifluoroacetyl-L-β-aspartyl-L-phenylalanine as a possible side product, although one cannot absolutely rule out its formation when the ring of the corresponding inner anhydride of aspartic acid is opened.

4. The Esters of α-Aspartylaminomalonic Acid

The asymmetric diesters of α-aspartylaminomalonic acid, synthesised by Japanese investigators[112–116], are outstanding among all known sweet compounds by exhibiting the highest level of sweetness. In general aminomalonic acid is unique in the sense that it forms particularly sweet derivatives, occupying either *N*- or C-terminal positions in the dipeptide. For example, the closest analogue of aspartame—the methyl ester of DL-aminomalonyl-L-phenylalanine—surpasses it as regards the intensity of its sweet taste (156–237 units)[112].

Analysis of experimental data[112–116] showed that the ester groups of the aminomalonate must differ significantly from one another in size (Table 5). The sweetest compounds obtained are those in which one of the ester groups is OMe. Specific requirements must be met by the second ester group, since it is responsible for the hydrophobic binding to the receptor. When the R^2 groups in compounds of the type

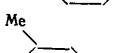
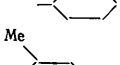
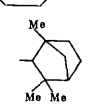


are replaced, the intensity of the sweet taste increases in the following sequence of R^2: aliphatic alkyl < cycloalkyl < cycloalkyl monosubstituted in the 2-position < phenyl. The

introduction of a substituent into any position in the cyclohexyl ring other than the 2-position or an increase of the number of substituents reduce the degree of sweetness[47].

Since all the compounds obtained were racemic mixtures with respect to the aminomalonic residue, it is still not clear which optical isomers in fact exhibit a sweet taste. In order to predict the taste of dipeptide esters, their projection formulae have been compared[117] with those of sweet and non-sweet standards, namely aminoacids, and it was concluded that, in the group of α-aspartylaminomalonic esters, the L–L-isomers should be sweet. This hypothesis has been confirmed by literature data[118].

Table 5. Derivatives of the aminomalonic acid.

L-α-Asp-DL-Ama-OR^1 (OR^2)			
R^1	R^2	RS	References
Me	iso-Pent	500	[115]
Me		300—600	[47, 112, 115]
Me		556—880	[47, 112, 115]
Me	 (*trans*)	5 450—7 300	[47, 112, 116]
Me		22 200—33 200	[47, 112, 113, 114]
Et		128—156	[47]
Et		192—284	[47]
Et	 (*trans*)	524—648	[47]
E		4 200—5 400	[47, 114]

As regards the methyl ester of aminomalonylphenylalanine, some workers[117] believe that the D–L-isomer is sweet, since its conformation agrees best with the receptor model, while others[118] give preference to the L–L-isomer by analogy with aspartame. Studies in this field are being continued and, as soon as the optically pure forms of the above dipeptides are isolated, the discrepancies will be resolved.

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It has been shown that the assortment of sweeteners based on aminoacids is fairly wide, their advantages over glucose are in certain aspects incontrovertible, and it may be hoped that in due course universal flavouring agents, meeting most successfully the requirements imposed on synthetic sucrose substituents, will be selected from the above large list and incorporated in the food industry.

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Diazadiphosphetidines

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The methods of synthesis and certain chemical properties of four-membered rings containing alternating nitrogen and phosphorus atoms with different degrees of coordination are examined. Attention is drawn to studies on the structure of diazadiphosphetidine rings by ^{31}P NMR and X-ray diffraction.
The bibliography includes 108 references.

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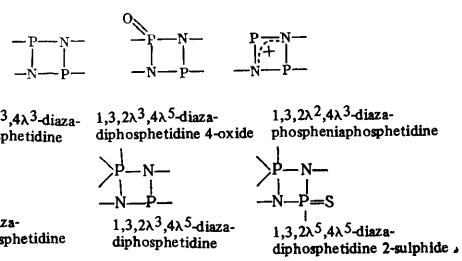
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I. INTRODUCTION

Phosphorus forms extremely readily four-membered cyclic compounds with other atoms. Rings are known in which there are alternating phosphorus and sulphur, phosphorus and silicon, phosphorus and boron, phosphorus and aluminium, and phosphorus and transition metal atoms. The derivatives of four-membered nitrogen- and phosphorus-containing heterocycles are particularly numerous and important[1-6]; compounds of this class were discovered a long time ago by Michaelis[7,8]. Since the publication of Kirsanov and Zhmurova's report in 1959 concerning the synthesis of dimeric trichlorophosphazoaryls[9], a new period has begun in the study of four-membered nitrogen–phosphorus heterocycles, mainly with phosphorus(V) atoms.

Considerable advances have been made in recent years in the development of methods for the synthesis and investigation of the structure (by ^{31}P and ^{19}F NMR and X-ray diffraction) and reactivity of four-membered heterocycles with phosphorus(III) atoms and also with phosphorus atoms having other types of coordination.

There is no unanimity concerning the nomenclature of compounds of this kind, but according to the IUPAC nomenclature[10] they should be referred to as diazadiphosphetidines:



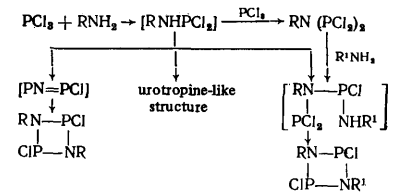
In 1970 we published a review on the chemistry of four-membered rings with alternating nitrogen and phosphorus atoms[11]. The present review includes the literature for the period from 1969 to the first half of 1978 inclusive.

II. SYNTHESIS OF DIAZADIPHOSPHETIDINES

1. Diazadiphosphetidines with Phosphorus(III) Atoms

One of the most universal methods of synthesis of diazadiphosphetidines is the reaction of amines or their hydrochlorides with PCl_3, alkyl- and aryl-dichlorophosphines, phosphoramidodichloridites, and alkyl phosphorodichloridites.

The synthesis of 1,3,2λ³, 4λ³-diazadiphosphetidines from PCl_3 can proceed via two pathways depending on the reaction conditions—in the presence of an excess of PCl_3 or with equimolar proportions of the reactants:

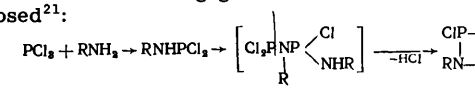


This mechanism has been confirmed by the results of a number of studies. The reaction of anilines or their hydrochlorides with an excess of PCl_3 at temperatures up to 30 °C leads to bisdichlorophosphinoalkyl(aryl)amines[12,13]. When bisdichlorophosphinoarylamines are heated to 100–150 °C, PCl_3 is split off and an unstable iminochlorophosphine, which rapidly dimerises, is apparently formed[14]. It has been recommended[15] that diazadiphosphetidines be synthesised from a mixture of arylamine hydrochloride and PCl_3 by refluxing for several hours in a suitable solvent, for example in *sym*-tetrachloroethylene. The interaction of phosphorus trichloride with methylamine yields a compound with a urotropine-like structure, while the reaction with sterically hindered higher alkylamines produces the corresponding diazadiphosphetidines[16-19].

The reaction of one mole of PCl_3 with three moles of lower alkylamines leads to a mixture of bisdichlorophosphinoalkylamine and 1,3-dialkyl-2,4-dichlorodiazadiphosphetidine, which are difficult to separate, but the cyclic compounds obtained in the reactions with propyl- and t-butylamines can be readily isolated by distillation. When PCl_3 interacts with t-butylamine or its hydrochloride, the reaction mixture contains t-butyl phosphoramidodichloridite in addition to the diazadiphosphetidine[19]. The reaction of PCl_3 with four-moles of t-butylamine gives rise only to a diazadiphosphetidine which is asymmetric with respect to the phosphorus atoms[20]:

$$2PCl_3 + 8t\text{-}C_4H_9NH_2 \rightarrow \begin{matrix} t\text{-}C_4H_9N\text{——}PCl \\ | \quad\quad | \\ t\text{-}C_4H_9NHP\text{—}NC_4H_9\text{-}t \end{matrix} + 5t\text{-}C_4H_9NH_2 \cdot HCl .$$

When this reaction was carried out in the presence of an excess of t-butylamine, the complete aminolysis product was isolated[20]. Since t-butyl phosphoramidodichloridite condenses to the corresponding diazadiphosphetidine in the presence of triethylamine, the following general reaction mechanism can be proposed[21]:



This course of the reaction is promoted by the presence of bulky substituents at the nitrogen atom[20]. Alkyl phosphorodichloridites can be made to undergo a similar reaction with PCl_3:

$$ROPCl_2 + ArNH_2 \rightarrow \begin{matrix} ROP{-}NAr \\ | \quad | \\ ArN{-}POR \end{matrix}.$$

It is noteworthy that Mitsunobu and Mukaijama[22], who obtained these compounds for the first time, attributed to them the structure of alkyl phenyliminophosphites and that their true structure was demonstrated by Kawashima and Inamoto using ^{31}P NMR and mass spectrometry[23].

The interaction of *N,N*-dialkylphosphoramidous dichlorides with aniline yielded 2,4-dianilino-1,3-diphenyldiazadiphosphetidine[24,25]:

$$R_2NPCl_2 + C_6H_5NH_2 \rightarrow \begin{matrix} C_6H_5NHP{-}NC_6H_5 \\ | \quad | \\ C_6H_5N{-}PNHC_6H_5 \end{matrix}.$$

Sulphonamides can be used in this reaction instead of aniline. Thus the reaction with tolunene-4-sulphonamide in pyridine gave a high yield of 2,4-bis(dimethylamino)-1,3-bis(toluene-4-sulphonyl)diazadiphosphetidine[26]:

$$ArSO_2NH_2 + (CH_3)_2NPCl_2 \rightarrow \begin{matrix} ArSO_2N{-}PN(CH_3)_2 \\ | \quad | \\ (CH_3)_2NP{-}NSO_2Ar \end{matrix}.$$

Asymmetric diazadiphosphetidines substituted at the nitrogen atoms are also synthesised by the reaction of bis-(dimethylaminochlorophosphino)methylamine or bis(dichlorophosphino)methylamine with t-butylamine[15,27]:

$$(CH_3)_2N{-}P(Cl){-}N(CH_3){-}P(Cl){-}N(CH_3)_2 \quad (CH_3\text{ on }N) + 3t\text{-}C_4H_9NH_2 \rightarrow \begin{matrix} (CH_3)_2NP{-}NC_4H_9\text{-}t \\ | \quad | \\ t\text{-}C_4H_9N{-}PN(CH_3)_2 \end{matrix}.$$

The reactions of diamides with dichlorophosphines or with PCl_3, which proceed via a similar mechanism, are similar to the above. When the bis(dimethylamide) of t-butylphosphonus acid was allowed to react with t-butyldichlorophosphine in the presence of triethylamine, the product was a phosphonamidous chloride, which was converted by phenyllithium into a mixture of the *cis*- and *trans*-isomers of 2,4-di-t-butyl-1,3-dimethyldiazadiphosphetidine[28]:

$$t\text{-}C_4H_9P(NHCH_3)_2 + m\ t\text{-}C_4H_9PCl_2 \xrightarrow{(C_2H_5)_3N} \rightarrow \begin{matrix} CH_3 \\ | \\ N \\ / \quad \backslash \\ t\text{-}C_4H_9P \quad PC_4H_9\text{-}t \\ | \quad\quad | \\ NHCH_3 \quad Cl \end{matrix} \xrightarrow{C_6H_5Li} \begin{matrix} t\text{-}C_4H_9P{-}NCH_3 \\ | \quad | \\ CH_3N{-}PC_4H_9\text{-}t \end{matrix}.$$

This mixture could be resolved into the individual isomers. The same method was used to obtain 1,3-di-t-butyl-4-chloro-2-methyl- and 1,3-di-t-butyl-2,4-dimethyl-diazadiphosphetidines[29].

It is noteworthy that the reaction of methylphosphonous di(t-butylamide) with PCl_3 takes place stereospecifically and leads to only the *cis*-isomer[29].

The considerable successes in the synthesis of diazaphosphetidines with phosphorus(III) in recent years have been associated with the application of trimethylsilylated amines. It has been shown[14,20,30] that heptamethyldisilazane and hexamethylphenyldisilazane react with PCl_3 in 1:1 proportions to form methyl- and phenyl-bisdichlorophosphinoamines. In the presence of an excess of the disilazanes, the reaction proceeds to 2,4-dichloro-1,3-dimethyl- or 2,4-dichloro-1,3-diphenyl-diazadiphosphetidines:

$$PCl_3 + RN[Si(CH_3)_3]_2 \rightarrow (Cl_2P)_2NR \xrightarrow{RN[Si(CH_3)_3]_2} \begin{matrix} ClP{-}NR \\ | \quad | \\ RN{-}RCl \end{matrix}.$$

The reaction of lithium t-butyltrimethylsilylamide with PCl_3 yielded 1,3-di-t-butyl-2,4-dichloro-1,3,2λ^3,4λ^3-diazadiphosphetidine[20,21]:

$$t\text{-}C_4H_9N(Li)Si(CH_3)_3 + PCl_3 \xrightarrow[-SiCl(CH_3)_3]{-LiCl} \begin{matrix} ClP{-}NC_4H_9\text{-}t \\ | \quad | \\ t\text{-}C_4H_9N{-}PCl \end{matrix}.$$

The lithium derivatives of *N,N*-dimethyl- and *N'*-trimethylsilylhydrazine are readily converted into the corresponding diazadiphosphetidines by reaction with *N*-t-butyl-*N*-methylphosphoramidous dichloride[31]:

$$(CH_3)_2NN(Li)Si(CH_3)_3 + Cl_2PN(CH_3)C_4H_9\text{-}t \xrightarrow[-Si(CH_3)_3Cl]{-LiCl,} \rightarrow \begin{matrix} t\text{-}C_4H_9 \\ \diagdown \\ NP{-}NN(CH_3)_2 \\ | \quad | \\ CH_3 \quad CH_3 \\ | \quad | \\ (CH_3)_2NN{-}PN \\ \diagup \\ C_4H_9\text{-}t \end{matrix}.$$

In the thermolysis of *N,N',N'*-tri-isopropyl-*N*-trimethylsilylphosphorodiamidous chloride, chlorotrimethylsilane is split off and a mixture of the *cis*- and *trans*-isomers of a substituted diazadiphosphetidine is formed[32]:

$$\begin{matrix} Cl\ Si(CH_3)_3 \\ | \quad | \\ (iso\text{-}C_3H_7)_2NP{-}NC_3H_7\text{-}iso \end{matrix} \xrightarrow[-Si(CH_3)_3Cl]{\Delta} \begin{matrix} (iso\text{-}C_3H_7)_2N{-}P{-}NC_3H_7\text{-}iso \\ | \quad | \\ iso\text{-}C_3H_7N{-}PN(C_3H_7\text{-}iso)_2 \end{matrix}.$$

Coordination-unsaturated aminoiminophosphines have been used successfully in the synthesis of diazadiphosphetidines. For example, *N,N',N'*-tris(trimethylsilyl)aminoiminophosphine and *N,N*-di-isopropyl-*N'*-trimethylsilylaminoiminophosphine dimerise to the corresponding diazadiphosphetidines[33,34]:

$$RR'NP{=}NSi(CH_3)_3 \rightarrow \begin{matrix} RR'NP{-}NSi(CH_3)_3 \\ | \quad | \\ (CH_3)_3SiN{-}PNRR' \end{matrix}.$$

N,N,N''-Tris(trimethylsilyl)-*N'*-methylhydrazinoiminophosphine, which exists in solution and in the gas phase as the monomer, dimerises to the diazadiphosphetidine after the removal of the solvent[34]:

$$[(CH_3)_3Si]_2NNP{=}NSi(CH_3)_3 \quad (CH_3\text{ on }N) \xrightleftharpoons[\text{solution or gas phase}]{\text{solid phase}} \begin{matrix} [(CH_3)_3Si]_2N{-}P{-}N{-}Si(CH_3)_3 \\ | \quad | \\ (CH_3)_3SiN{-}PNN[Si(CH_3)_3]_2 \\ | \\ CH_3 \end{matrix}.$$

Certain other syntheses of diazadiphosphetidines apparently also involve the intermediate formation of aminoiminophosphines, for example, in the reaction of bis-*N,N*-dimethylphosphorodiamidous chloride with the sodium salt of hexamethyldisilazane[35-37]:

$$[(CH_3)_2N]_2PCl + NaN[Si(CH_3)_3]_2 \xrightarrow{-NaCl} [(CH_3)_2N]_2P{-}N[Si(CH_3)_3]_2 \xrightarrow{-(CH_3)_3NSi(CH_3)_2} \rightarrow [(CH_3)_2N{-}P{=}NSi(CH_3)_3] \rightarrow \begin{matrix} (CH_3)_2N{-}P{-}NSi(CH_3)_3 \\ | \quad | \\ (CH_3)_3SiN{-}PN(CH_3)_2 \end{matrix}.$$

Arenesulphonamides react via a similar mechanism with substituted phosphorodiamidous chlorides in the presence of pyridine[26]:

$$ArSO_2NH_2 + C_5H_5N \rightleftarrows ArSO_2\bar{N}H + C_5H_5\overset{+}{N}H \xrightarrow{(RR^1N)_2PCl} \rightarrow ArSO_2NHP(NRR^1)_2 + Cl^- \xrightarrow[-HNRR^1]{C_5H_5N} [ArSO_2N{=}PNRR^1] \rightarrow \begin{matrix} ArSO_2N{-}PNRR^1 \\ | \quad | \\ RR^1NP{-}NSO_2Ar \end{matrix}.$$

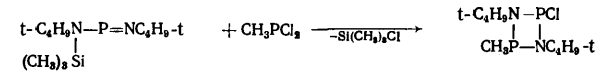
The thermal decomposition of phosphorous trianilide (110 °C, toluene) involves the elimination of one aniline molecule and the formation of the corresponding diazadiphosphetidine[38]:

$$(C_6H_5NH)_3P \rightarrow [C_6H_5N{=}P{-}NHC_6H_5] \rightarrow \begin{matrix} C_6H_5N{-}PNHC_6H_5 \\ | \quad | \\ C_6H_5NHP{-}NC_6H_5 \end{matrix}.$$

The formation of diazadiphosphetidines in the transamination of phosphorous triamides with substituted benzamidines belongs to the same group of reactions[39]:

$$C_6H_5C(NR)(NH_2) + (R_2N)_3P \rightarrow \begin{matrix} C_6H_5C{-}N{-}PNR_2 \\ \| \quad | \quad | \\ RNR_2NP{-}NCC_6H_5 \\ \quad\quad\quad\quad \| \\ \quad\quad\quad\quad NR \end{matrix}.$$

4-Chloro-2-methyldiazadiphosphetidine has been obtained by the reaction of *N,N'*-di-t-butyl-*N*-trimethylsilylaminoiminophosphine with methyldichlorophosphine[29]:

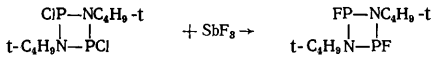


As a rule, $1,3,2\lambda^3,4\lambda^3$-diazadiphosphetidines are formed as mixtures of the *cis*- and *trans*-isomers, although certain diazaphosphetidines with bulky substituents at the nitrogen atoms are obtained in the *cis*-form[35]. After prolonged heating in 1,2-dichlorobenzene at 100 °C, the isomeric composition of the mixture changes towards an increase of the amount of the *trans*-isomer. Thus pure *cis*-2,4-bisdimethylamino-1,3-bistrimethylsilylaminodiazadiphosphetidine is converted into a mixture containing 30% of the *cis*-isomer and 70% of the *trans*-isomer[35].

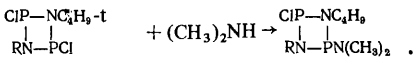
^{31}P NMR is a convenient method for the determination of the *cis*- and *trans*-structures of diazadiphosphetidines. The signal in the region of ~−100 p.p.m.corresponds to the *cis*-isomers while in the case of the *trans*-isomers the signal shifts downfield (to between −180 and −220 p.p.m.)[23,33,35].

In the series of 1,3- or 2,4-di-t-butyl derivatives the ^{31}P NMR signal also shifts markedly downfield. The ^{31}P NMR signal of *cis*-1,3-di-t-butyl-2,4-dichlorodiazadiphosphetidine is at −210.9 p.p.m.[20] The ^{31}P NMR spectra of 2,4-di-t-butyl-1,3-dimethyldiazadiphosphetidine contain signals with chemical shifts of −210.7 p.p.m. (*cis*-isomer) and −281.7 p.p.m. (*trans*-isomer)[40].

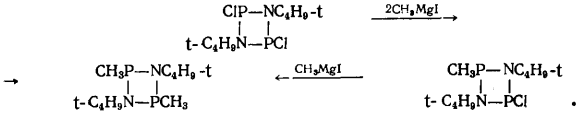
The following group of methods of synthesis of $1,3\text{-}2\lambda^3,4\lambda^3$-diazadiphosphetidines consists of reactions involving the substitution of halogen atoms by nucleophiles or electrophiles. 2,4-Dichlorodiazadiphosphetidines exchange[41] chlorine atoms for fluorine on treatment with SbF_3:



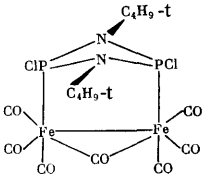
Chlorine atoms are also readily substituted by different nucleophiles. Thus, when 1,3-di-t-butyl-2,4-dichlorodiazadiphosphetidine is treated with an excess of dimethylamine, a mixture of the corresponding *cis*- and *trans*-isomers is formed[15]. The reaction with diethylamine or t-butylamine yields only the *cis*-isomer. Following the interaction with two moles of dimethylamine, the product of the substitution of only one chlorine atom was obtained[15]:



1,3-Di-t-butyl-2,4-dichloro-1,3,2,4-diazadiphosphetidine and 1,3-di-t-butyl-2-chloro-4-methyl-1,3,2,4-diazadiphosphetidine react with methylmagnesium iodide to form 2,4-dimethyldiazadiphosphetidine[29]:



As phosphorus(III) derviatives, diazadiphosphetidines form complexes with metal carbonyls. The interaction of iron nonacarbonyl with 1,3-di-t-butyl-2,4-dichlorodiazadiphosphetidine in tetrahydrofuran (THF) yielded a derivative of iron heptacarbonyl[42]:

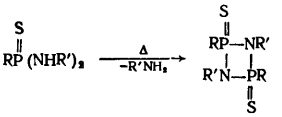


Relative to the initial diazadiphosphetidine, the ^{31}P NMR spectrum of this compound shows an upfield shift of the signal from −207 p.p.m. to +17 p.p.m.[36]

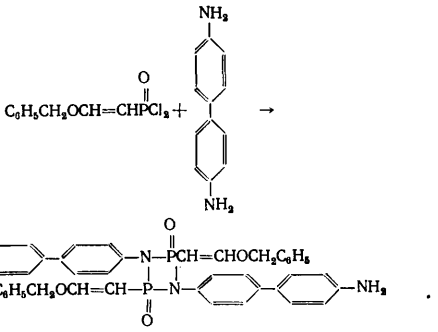
The complexes obtained from a single molecule of 2,4-bisdimethylamino-1,3-bistrimethylsilyldiazadiphosphetidine and two molecules of chromium or molybdenum pentacarbonyl have the *trans*-arrangement of the substituents[36]. Relative to $1,3,2\lambda^3,4\lambda^3$-diazadiphosphetidine, the ^{31}P NMR spectra of these compounds show a shift of the signal from −107.6 p.p.m. to −155 and −131 p.p.m. respectively[42].

2. Diazadiphosphetidines with Tetracoordinate Phosphorus Atoms

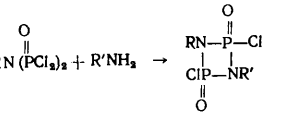
The traditional method of synthesis of diazadiphosphetidines with phosphorus(V) atoms is the pyrolysis of the di- and triamides of phosphorus acids[11]. This method has been used to obtain isomeric 1,3-diethyl-2,4-diphenyl- [43,44] and 1,2,3,4-tetraphenyl-$1,3,2\lambda^5,4\lambda^5$-diazadiphosphetidine 2,4-disulphides[45]:



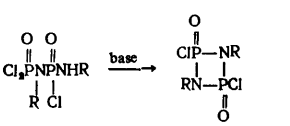
The second traditional method involves the reaction of phosphorus acid dichlorides with primary amines or anilines[11]. It has been used[46] to synthesise 1,3-bis[4-(4-aminophenyl)-phenyl]-2,4-bis(benzyloxyvinyl)-$1,3,2\lambda^5,4\lambda^5$-diaza -diphosphetidine 2,4-dioxide:



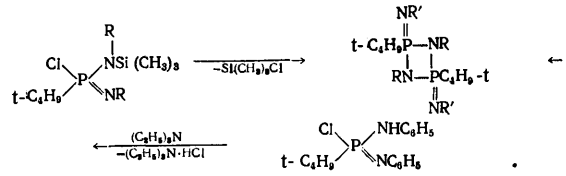
By developing this reaction, a method has been devised for the synthesis of asymmetrically 1,3-disubstituted diazadiphosphetidine 2,4-dioxides by the cyclisation of *N*-alkyl-(aryl)-*N,N*-bis(dichlorophosphono)amines under the influence of primary amines[19,27]:



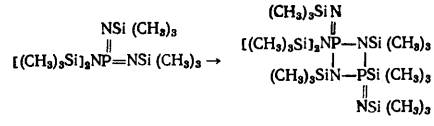
The reaction with thiophosphono-derivatives proceeds with much more difficulty. In all cases mixtures of *cis*- and *trans*-isomers are formed. Acyclic diphosphazans can be converted into diazadiphosphetidines under the influence of bases[20]:



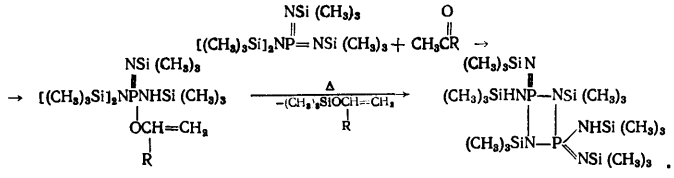
Derivatives of diazadiphosphetidine 2,4-di-imide have been obtained from substituted phosphonamidimidic chlorides[47]:



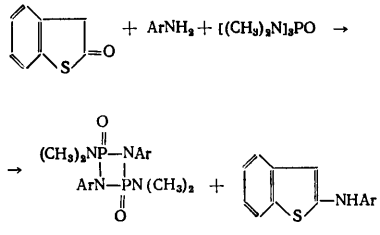
2,4-Diaminodiazadiphosphetidine 2,4-di-imide, fully silylated at the nitrogen atoms, is formed on dimerisation of the corresponding aminodi-iminophosphorane[48]:



In order to obtain hexakis(trimethylsilyl)diazadiphosphetidine, tetrakis(trimethylsilyl)aminodi-iminophosphorane is treated with acetone or acetophenone with subsequent elimination of trimethylsilyl vinyl ether and dimerisation *in vacuo* on heating[49]:

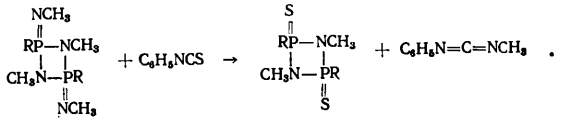


An interesting method for the synthesis of 1,3-diaryldiazaphosphetidine 2,4-dioxides involves the interaction of 2-oxodihydrobenzo[*b*]thiophen and anilines in hexamethylphosphoramide[50]; the yield of the final products is 70–80%:

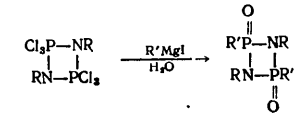


Other methods for the synthesis of diazadiphosphetidine 2,4-dichalcogenides, 2,4-di-imides, and 2,4-imidoximes involve addition or substitution reactions with the phosphorus atoms of the diazadiphosphetidine ring. Reactions involving the addition of sulphur, selenium, tellurium[29,35,40] and trimethylsilyl azide as well as the oxidation of 1,3,2λ^3,4λ^3-diazadiphosphetidines by nitrogen oxides or dimethyl sulphoxide lead to the corresponding diazadiphosphetidine 2,4-disulphides, 2,4-diselenides, 2,4-ditellurides, 2,4-di-imides, and 2,4-dioxides in high yields.

The conversion of diazadiphosphetidine 2,4-di-imide into the corresponding diazadiphosphetidine disulphide on treatment with phenyl isothiocyanate is unusual; even if the individual *cis*- and *trans*-isomers of the di-imide are introduced into the reaction, the final product is a mixture of isomers[47]:



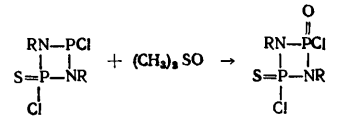
The reaction of 1,3-diphenyl- or 1,3-di-*m*-tolyl-hexachlorocyclodiphosphazanes with ethyl- or phenyl-magnesium iodide and subsequent decomposition with water yielded the corresponding diazadiphosphetidine 2,4-dioxides (yield 48–69%)[51].



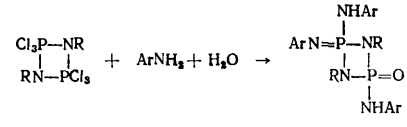
Ethylmagnesium iodide reacts similarly with 1,3-di-*o*-chlorophenyl- and di-*o*-tolyl-hexachlorodiazadiphosphetidines, but, apart from the corresponding dioxides, small amounts of 1,3-di-*o*-chlorophenyl-2,2,4,4-tetraethyl-2,4-dihydroxydiazadiphosphetidine and 2,4,4-triethyl-4-hydroxy-1,3-di-*o*-tolyldiazadiphosphetidine 2-oxide are formed in small amounts[51].

The synthesis of diazadiphosphetidines 2,4-dichalcogenides asymmetric with respect to the phosphorus atoms has been described[20,51].

1,3,2λ^3,4λ^5-diazadiphosphetidine sulphides are readily oxidised by dimethyl sulphoxide to a mixture of the *cis*- and *trans*-isomers of diazadiphosphetidine 2-oxide 4-sulphides asymmetric with respect to phosphorus[20]:

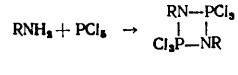


Diazadiphosphetidine 2-imide 4-oxides have been obtained by the aminolysis of hexachlorodiazadiphosphetidines by anilines in the presence of moisture[52]:

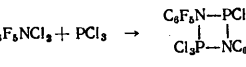


3. Diaxadiphosphetidines Containing Pentacoordinate Phosphorus Atoms

The Kirsanov reaction continues to play a notable role in the synthesis of 1,3,2λ^5,4λ^5-diazadiphosphetidines. Hexafluorodiazadiphosphetidines have been obtained by this method[53,54]:



Another interesting method for the synthesis of compounds of this kind is oxidative imination of phosphorus trichloride by *N*,*N*-dichloroperfluoroarylamines[55]:



The most interesting and important results in the study of the chemistry of diazadiphosphetidines with phosphorus(V) have been obtained in relation to fluorinated derivatives and polycyclic compounds containing the diazadiphosphetidine fragment.

Schmutzler and coworkers developed a number of novel methods for the synthesis of fluorodiazadiphosphetidines. The reaction of alkyl(aryl)tetrafluorophosphoranes or

dialkyl(diaryl)trifluorophosphoranes with heptamethyldisilazane constitutes a convenient method of synthesising fluorinated diazadiphosphetidines[56,57]:

$$RPF_4 + 2CH_3N[Si(CH_3)_3]_2 \rightarrow \begin{matrix} RF_2P{-}NCH_3 \\ | \quad | \\ CH_3N{-}PF_2R \end{matrix} + 4Si(CH_3)_3F \ .$$

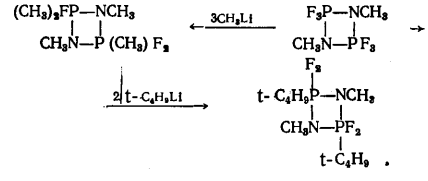
An asymmetric diazadiphosphetidine has also been obtained by this method[58]:

$$CH_3PF_2 + CH_3N[Si(CH_3)_3]_2 + C_6H_5N[Si(CH_3)_3]_2 \rightarrow \begin{matrix} CH_3F_2P{-}NCH_3 \\ | \quad | \\ C_6H_5N{-}PF_2CH_3 \end{matrix} \ .$$

Instead of disilazanes, one can use the lithio-derivatives of alkylamines[59]:

$$2RNLi_2 + 2R_2PF_3 \rightarrow \begin{matrix} R_2FP{-}NR \\ | \quad | \\ RN{-}PFR_2 \end{matrix} + 4LiF \ .$$

On reaction with organometallic compounds, hexafluoro-1,3-dimethyldiazadiphosphetidines exchange fluorine atoms for alkyl groups[57-59]:



It is of interest that, when a mixture of 1,2,3,4-tetramethyl- and 1,3-dimethyl-2,4-diphenyl-2,2,4,4-tetrafluorodiazadiphosphetidines is heated, a disproportionation reaction takes place and a compound asymmetric with respect to phosphorus is formed[58]:

$$\begin{matrix} F_2(CH_3)P{-}NCH_3 \\ | \quad | \\ CH_3N{-}P(CH_3)F_2 \end{matrix} + \begin{matrix} F_2(C_6H_5)P{-}NCH_3 \\ | \quad | \\ CH_3N{-}P(C_6H_5)F_2 \end{matrix} \rightarrow \begin{matrix} F_2(C_6H_5)P{-}NCH_3 \\ | \quad | \\ CH_3N{-}P(CH_3)F_2 \end{matrix} \ .$$

Appel et al. quite unexpectedly obtained a diazadiphosphetidine by the hydrofluorination of silylated bisiminophosphorane in trichlorofluoromethane[60]:

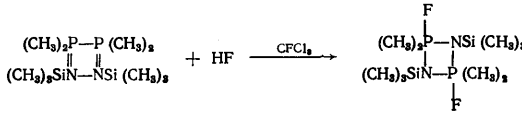


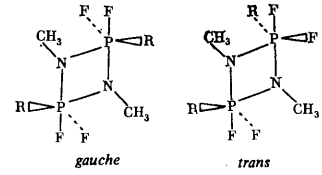
Table 1. The chemical shifts (δ, p.p.m.) of the *gauche*- and *trans*-isomers of 2,4-dialkyl-2,2,4,4-tetrafluoro-1,3-dimethyl-1,3,2,4-diazadiphosphetidines between −60° and −70 °C.[56]

Alkyl	CH_3	CH_2Cl	$CHCl_2$	CCl_3
gauche	−51.2	−56.9	−64.8	−59.0
trans	−47.4	−53.1	−62.1	−60.7

The signals in the ^{31}P NMR spectra of diazadiphosphetidines with phosphorus(V) are located in the region of 82.5–38.3 p.p.m., depending on the environment around the phosphorus atom[54]. It is noteworthy that, in a series of compounds of the type $(RF_2PNCH_3)_2$, the spin–spin coupling constant is directly related to the electronegativity of the ligand R:[61]

R	$(C_2H_5)_2N$	C_6H_5	C_6F_5	CCl_3
J_{P-P}, Az	140	111	80	125

Tetrafluorodiazadiphosphetidines can exist as *gauche*- and *trans*-isomers:



In the solid state they exist as the *trans*-isomers, while in solution there is equilibrium between the *gauche*- and *trans*-forms as a result of the pseudo-rotation at the phosphorus atom[56,57]. The *gauche*–*trans* equilibration process is rapid on the NMR time scale and the presence of the signals of the two isomers in the ^{31}P NMR spectra can be detected only at low temperatures (between −40° and −60 °C) (Table 1). It is noteworthy that in the series of 2,4-dialkyltetrafluorodiazadiphosphetidines the percentage content of the *trans*-isomer increases with increase of the degree of branching of the alkyl group (Table 2)[56,57].

Table 2. The ratio of the *gauche*- and *trans*-isomers of 2,4-dialkyl-2,2,4,4-tetrafluoro-1,3-dimethyl-1,3,2λ^5,4λ^5-diazadiphosphetidines[56,57].

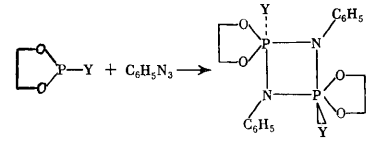
Alkyl	CH_3	C_2H_5	iso-C_3H_7	t-C_4H_9	CH_2Cl	$CHCl_2$	CCl_3
Content of *trans*-isomer, %	47	56	61	92	57	71	76

The thermal decomposition of hexahalogenodiazadiphosphetidines does not take place unambiguously. On heating, hexachloro-1,3-diethyldiazadiphosphetidine splits off methyl chloride and is convered into a polymer[62,63]:

$$x \begin{matrix} CH_3N{-}PCl_3 \\ | \quad | \\ Cl_2P{-}NCH_3 \end{matrix} \xrightarrow[48\ h]{200°} 2x\,CH_3Cl + (NPCl_2)_{2x} \ .$$

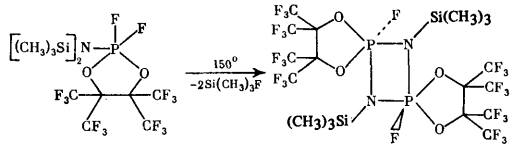
Its hexafluoro-analogue gives rise to a tetramer on heating in a sealed tube at 130 °C; in addition, a salt with the composition $(CH_3N)_4P_3F_6^+PF_6^-$ has been isolated from the residue[62-64].

Kabachnik, Gilyarov, and Tikhonina[65-68] carried out a detailed study of the conditions governing the formation of the diazadiphosphetidine ring from cyclic phosphites—derivatives of ethylene glycol, 1,2-propylene glycol, and catechol—under the conditions of the Staudinger reaction. It was shown that the amides of glycol phosphites react with phenyl azide to form phosphoramidimidates, while esters, thioesters, and fluoride are converted into tricyclic dispirodiazadiphosphetidines:

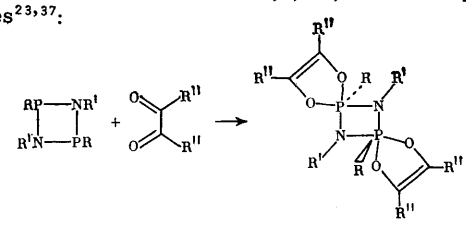


The presence of two signals in the ^{31}P NMR spectra, whose chemical shifts differ by 0.47–0.63 p.p.m., has been explained by the presence of two isomers, whose formation is caused by the pseudorotation at the phosphorus atom in solution.

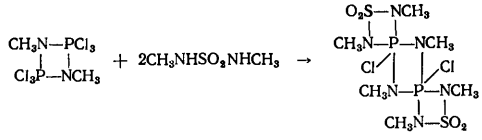
The same tricyclic system has been obtained[69] on heating bis(trimethylsilyl)aminoperfluoropinacolyldifluorophosphorane at 150 °C:



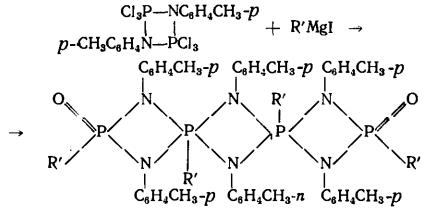
Tricyclic dispiro-1,3,2λ⁵,4λ⁵-diazadiphosphetidines are also formed when α-diketones add to 1,3,2λ³,4λ³-diazadiphosphetidines[23,37]:



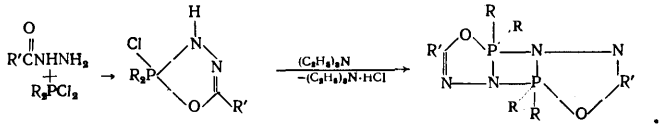
or on interaction of hexachloro-1,3-dimethyldiazadiphosphetidine with 1,3-dimethylsulphamide[70]:



or in the reaction of hexachloro-1,3-di-*p*-tolyldiazadiphosphetidine with ethyl- or phenyl-magnesium iodide[51]:

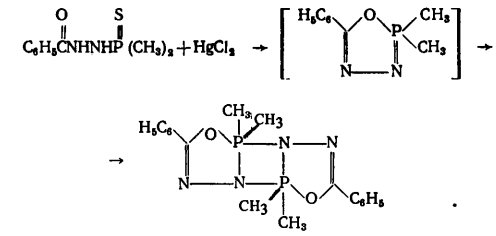


Interesting studies on the synthesis of condensed heterocyclic systems containing the diazadiphosphetidine ring have been carried out by Kabachnik and coworkers[65,66,69] and by Schmidpeter and coworkers[71–73]. As a result of the reaction of the chlorophosphoranes $(CH_3)_nPCl_{5-n}$ ($n = 0–2$), trichlorodiphenylphosphorane, and the chlorides of dimethyl- and diphenyl-phosphinic acids with acylhydrazines and subsequent treatement of the resulting 2-chloro-1,3,4,2-oxadiazaphospholines with triethylamine yielded the dimeric 1,3,4,2-oxa-azaphospholes. The latter constitute a tricyclic system with a diazadiphosphetidine fragment[71–73]:

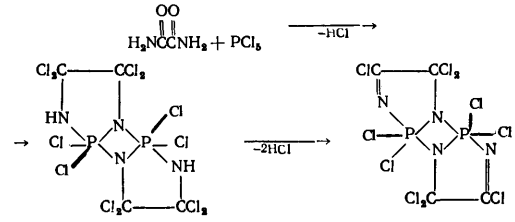


The halogen atoms at the phosphorus atom can be substituted by alkoxy- or phenoxy-groups.

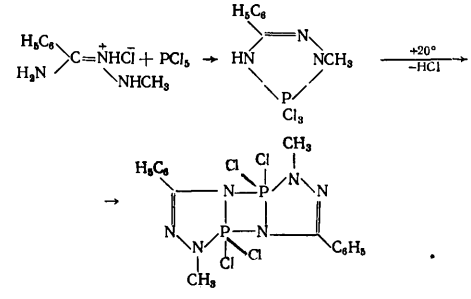
The same tricyclic system has been obtained on treating *N*-benzoyl-*N'*-dimethylphosphinothionylhydrazine with mercury(II) chloride and triethylamine. The reaction proceeds via the intermediate formation of 1,3,4,2-diazaphosphole with subsequent cyclodimerisation[74]:



Tricyclic systems with a similar structure, containing the diazaphosphetidine fragment, have been obtained by the interaction of oxamide with an excess of PCl_5 in dichloroethane at 50–55 °C:[75]

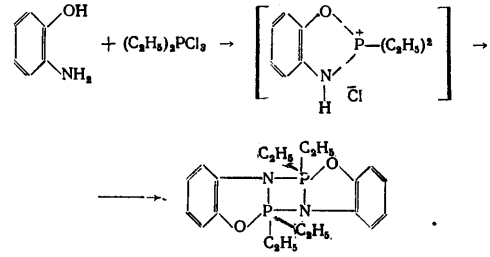


or by treating the hydrochloride of *N*-methylbenzamidrazone with PCl_5. When the reaction is carried out at 0°C, 3,3,3-trichloro-1,2,4-3λ⁵-triazaphosphole is formed. The latter splits off hydrogen chloride at 20 °C and is converted into a cyclic dimer[76]:

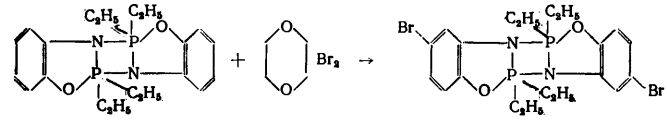


When *o*-aminophenol is treated with PCl_5 or R_2PCl_3, dimeric 1,3,2-oxazaphospholes are formed[65,77,78].

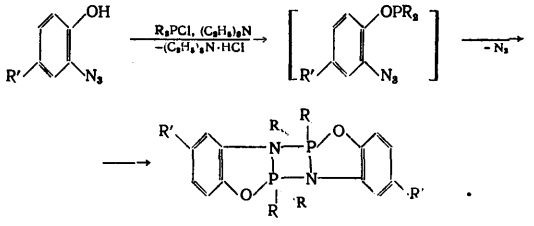
The hydrochloride of benzo-1,3,2-oxazaphosphole has been isolated as an intermediate in the reaction with chlorodiethylphosphorane. On treatment with triethylamine it is converted into the corresponding cyclic product[65]:



The *P,P,P',P'*-tetrachloro derivatives readily undergo reactions involving the substitution of chlorine atoms by alkoxy- and phenoxy-groups. The *P,P,P',P'*-tetraethyl derivatives is brominated by dioxan dibromide in the benzene ring[65]:

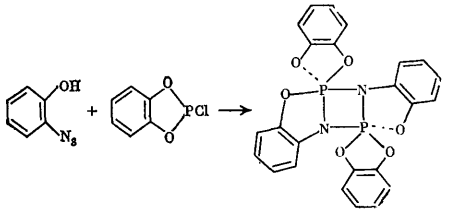


The same pentacyclic system has been obtained by the reaction of *o*-azidophenols with dialkylphosphorochloridites, dialkylchlorophosphines, and tetra-alkylphosphorodiamidous chlorides[65,66,79]:



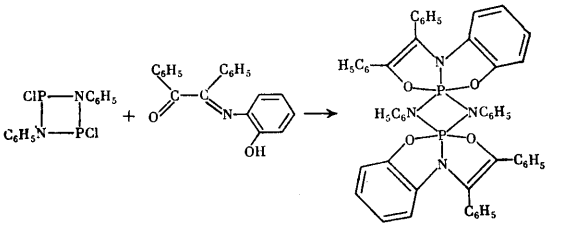
The first stage is carried out at 0 °C and the second (after separating triethylamine hydrochloride) at 20 °C.

When the phosphorochloridite of catechol is introduced into the reaction, a nonacyclic system is formed[66]:



The same system has been obtained also by interaction of *o*-aminophenol with *o*-phenylenedioxytrichlorophosphorane[66].

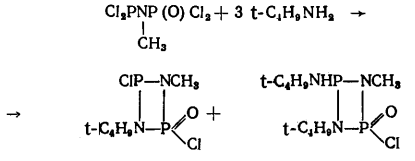
The reaction of 2,4-dichloro-1,3-diphenyl-1,3,2λ³,4λ³-diazadiphosphetidine with *o*-hydroxyphenyliminodibenzoyl leads to a pentacyclic phosphorane[80]:

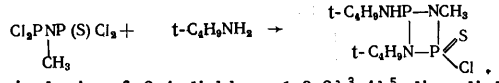


Its ^{31}P NMR spectrum has only one signal at −50.5 p.p.m., which agrees with the fact that the initial diazadiphosphetidine is in the *cis*-form and that substitution at both phosphorus atoms takes place stereospecifically[80].

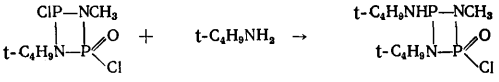
4. Diazadiphosphetidines Containing Tervalent and Tetracoordinate or Pentacoordinate Phosphorus Atoms

When *N*-(dichlorophosphino)-*N*-(dichlorophosphinoyl)-methylamine reacts with three moles of t-butylamine, a mixture of diazadiphosphetidine 4-oxides, differing in the degree of substitution of chlorine atoms at phosphorus(III), is formed. When *N*-(dichlorophosphino)-*N*-(dichlorothiophosphinoyl)methylamine is treated with t-butylamine, a 10 : 1 mixture of isomers of diazadiphosphetidine 2-sulphide is produced[27]:



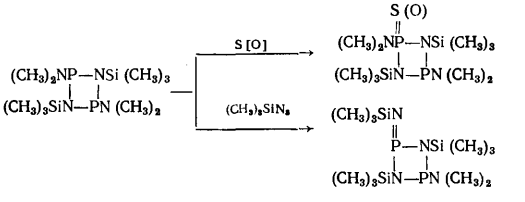


The aminolysis of 2,4-dichloro-1,3,2λ³,4λ⁵-diazadiphosphetidine 2-oxide and 2-sulphide (as mixtures of isomers) by t-butylamine results in the substitution of a chlorine atom at phosphorus(III) and the isomeric composition of the products is altered: the cause of the latter phenomenon is hitherto unknown[27]:

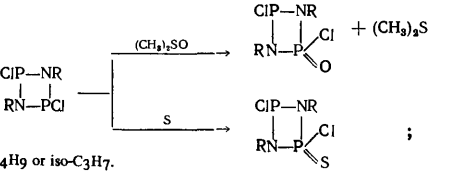


The coordination-unsaturated *N*,*N*,*N*′-tris(trimethylsilyl)-aminoiminophosphine undergoes the (2 + 2)-cycloaddition reaction with tetrakis(trimethylsilyl)aminodi-iminophosphorane and gives rise to a substituted 1,3,2λ³,4λ⁵-diazadiphosphetidine[81]. Structural data suggest that the unshared electron pair at the phosphorus atoms in diazadiphosphetidines has an appreciable amount of *s* character[82,83]. Diazadiphosphetidines containing two phosphorus(III) atoms combine under mild conditions with one mole of sulphur, selenium, or tellurium, giving rise to the corresponding asymmetric diazadiphosphetidine 4-sulphides, 4-selenides, or 4-tellurides[29,34,83,84].

2,4-Bisdimethylamino-1,3-bis(trimethylsilyl)-1,3,2λ³,4λ⁴-diazadiphosphetidine can be oxidised selectively by sulphur, oxygen, or trimethylsilyl azide[29]:



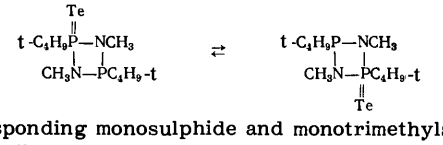
The isopropyl and *s*-butyl derivatives of 1,3,2λ³,4λ³-diazadiphosphetidines undergo controlled oxidation by dimethyl sulphoxide and sulphur with formation of diazadiphosphetidine 2-oxides and 2-sulphides[20]:



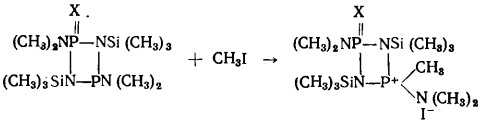
R = t-C$_4$H$_9$ or iso-C$_3$H$_7$.

These compounds are thermally stable and can be purified by vacuum distillation.

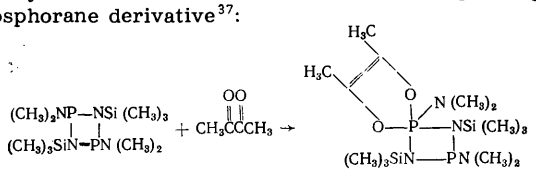
A study of the temperature variation of the ^{1}H and ^{31}P NMR spectra of *cis*-2,4-di-t-butyl-1,3-dimethyl-1,3,2λ³,4λ⁵-diazadiphosphetidine 4-telluride demonstrated the existence of the dynamic equilibrium[84]



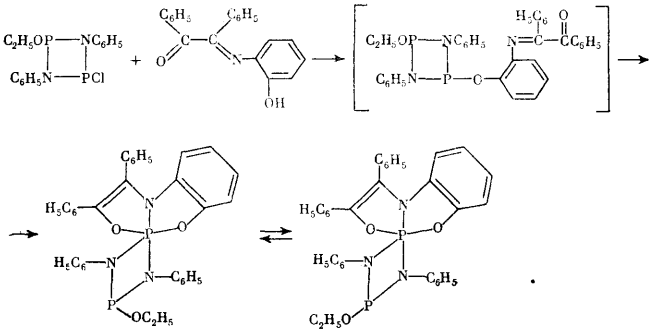
The corresponding monosulphide and monotrimethylsilylimide are readily alkylated by methyl iodide and give rise to derivatives of 1,3-diaza-2-phosphonia-4-phosphetidine[35]:



The reaction of 2,4-bis(dimethylamino)-1,3-bis(trimethylsilyl)-1,3,2λ³,4λ³-diazadiphosphetidine with 1 mole of diacetyl results in the formation of the corresponding monophosphorane derivative[37]:

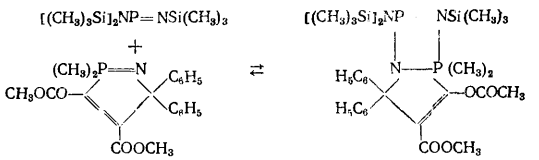


A similar reaction was observed also in the case of *o*-hydroxyphenyliminodibenzoyl[80]:

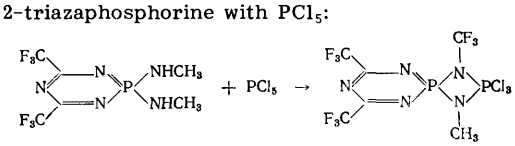


The tricyclic product exists as a mixture of *cis*- and *trans*-isomers. The chlorine atom is probably initially substituted and this is followed by intramolecular cycloaddition[80].

The addition of an azaphosphole (a cyclic product) to aminoiminophosphine yielded a bicyclic adduct, which exists in chloroform solution in equilibrium with the initial compounds. At 70 °C the equilibrium is 60% displaced to the left[91]:

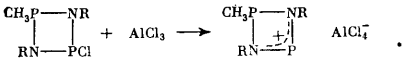


A spiro-compound containing six- and four-membered rings has been obtained[85] by the reaction of 2,2-bis(methylamino)-1,3,5,2-triazaphosphorine with PCl_5:



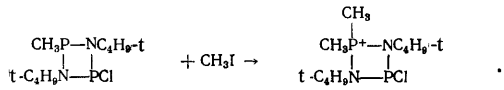
5. Diazaphosphenia- and Diazaphosphonia-phosphetidines

2-Choro-4-methyl-1,3,2,4-diazadiphosphetidine reacts with aluminium chloride to form a zwitter-ionic phosphenium salt—a new representative of the class of substances containing dicoordinate phosphorus ions:



The phosphenium salt is insoluble in ether, pentane, and benzene, but is readily soluble in CH_2Cl_2 and CH_3CN. In its ^{31}P NMR spectrum the doublet with a chemical shift of −252.0 p.p.m. ($^2J_{P-P} = 36$ Hz) is due to the dicoordinate phosphorus atom[29,86], while the doublet with a chemical shift of −201 p.p.m. refers to the phosphorus(III) atom.

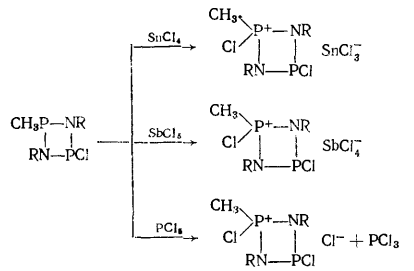
The reaction of 2,4-dimethyl- or 2-chloro-4-methyl-1,3,2,4-diazadiphosphetidine with electrophilic alkyl halides (methyl iodide or bromide, ethyl bromide) leads to cyclic phosphonium salts containing phosphonium and phosphine phosphorus atoms[29]:



Cyclic diazaphosphoniaphosphetidine salts have also been obtained by the alkylation of 2,4-bis(dialkylamino)-1,3-bis(trimethylsilyl)-1,3,2λ³,4λ⁵-diazadiphosphetidines with an excess of methyl iodide at −70 °C. Their isomeric composition was investigated by ^{31}P and ^1H NMR; the reaction products are in most cases pure *cis*-isomers; after they have been heated at 100–130 °C for three days, the *trans*-isomer predominates in the mixture[35].

The ^{31}P NMR spectra of diazaphosphoniaphosphetidines show two signals: in a low field due to the phosphorus(III) atom and in a high field due to the phosphorus(V) atom[29]. The ^{31}P NMR spectra of methylphosphoniaphosphetidine iodides, which are mixtures of *cis*- and *trans*-isomers, contain four signals: −26.2—−33.8 p.p.m. (P^{IV}), −86.5—−97.6 p.p.m. (P^{III}), and $J_{P-P} = 33$–38 Hz for the *cis*-isomer and −50.6—−54.3 p.p.m. (P^{IV}), −120.7—−137.6 p.p.m. (P^{III}), and $J_{P-P} = 20$–33 Hz for the *trans*-isomer[35].

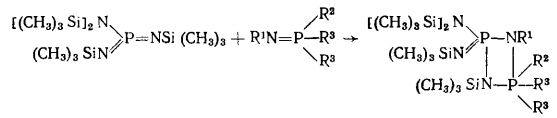
Diazoniaphosphetidine salts are also formed in the reaction of 1,3-di-t-butyl-2-chloro-4-methyl- or 2,4-dimethyl-1,3,2,4-diazadiphosphetidines with Lewis acids ($SbCl_5$, $SnCl_4$, and PCl_5). In all cases 1 : 1 adducts are formed initially and these then rearrange to the salts; the PCl_4^- anion decomposes under these conditions to PCl_3 and Cl^-: [86]



The ^{31}P NMR spectra of these compounds contain doublet P^{IV} signals in the range between −70 and −80.0 p.p.m.

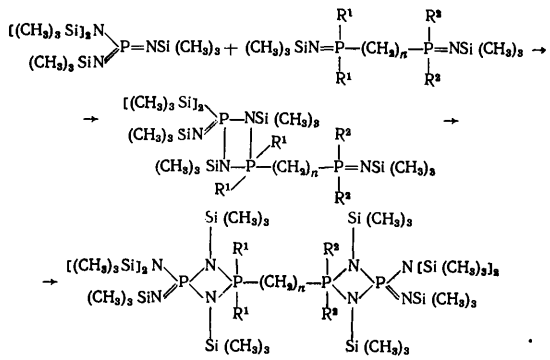
6. Diazadiphosphetidines with Tetracoordinate and Pentacoordinate Phosphorus Atoms

Diazadiphosphetidines with phosphorus(IV) and phosphorus(V) atoms are obtained mainly by the (2 + 2)-cycloaddition of phosphine imides to *N,N,N',N'*-tetrakis(trimethylsilyl)aminodi-iminophosphorane[33,87,88]:



A number of other phosphine imines[89] as well as labelled [^{15}N]*N*-methyltris(dimethylamino)phosphine imide[90] have been introduced into this reaction. The above cyclisation

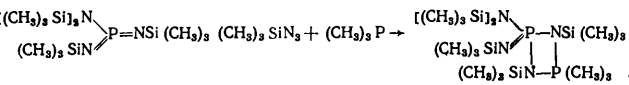
principle has been transferred also to alkylenebisphosphine imides[88]:



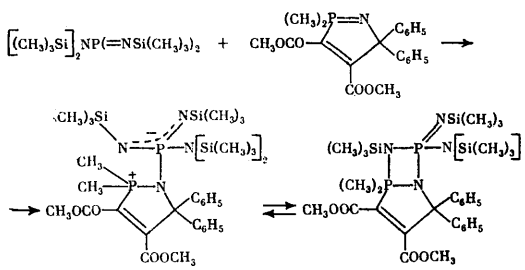
N-t-Butyltriphenylphosphine imide and tris(dimethylamino)-*N*-trimethylsilylphosphine imide do not undergo this reaction even after heating for many hours.

For the silylated methylenebis(methylphenylphosphine imide), it is possible to achieve a controlled addition, to isolate the asymmetric product, and then to convert it into a symmetrical alkylenebis(diazadiphosphetidine). 1,4-Butylene derivatives give rise to symmetrical products only[90].

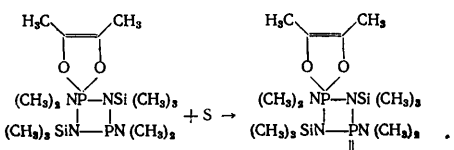
An interesting modification of the reaction involves the heating of the adduct of trimethylsilyl azide and silylated aminodi-iminophosphorane with trimethyl- and triphenylphosphines[88]:



The reaction of azaphosphole with aminodi-iminophosphorane yielded a bicyclic adduct resulting from (2 + 2)-cycloaddition:



On heating in solution, the adduct is reversibly converted into a dipolar ion[91]. A diazadiphosphetidine with a P=S group has been synthesised[37] by the addition of sulphur to the corresponding phosphorus(III) derivative:



III. THE STRUCTURE OF THE DIAZADIPHOSPHETIDINE RING

The structure of the diazadiphosphetidine ring has been investigated by various physicochemical methods, but X-ray diffraction analysis proved to be the most informative.

The structure of 1,3-di-t-butyl-2,4-dichloro-1,3,2λ^3,4λ^3-diazadiphosphetidine has been investigated by X-ray diffraction[92]. The P–N bond length is 1.689 Å, which corresponds to the bond length in dimethylphosphoramidous dichloride (1.69 Å) and indicates partial p_π–d_π bonding[93]. The chlorine atoms are in the *cis*-configuration. The ring in the molecule is not planar, its atoms deviating in succession from the plane of the ring by 0.045 Å. In the molecule of *trans*-1,3-bis(trimethylsilyl)-2,4-di[bis(trimethylsilyl)amino]-1,3,2λ^3,4λ^5-diazadiphosphetidine the P–N bond length (1.727 Å) [33] approaches that of a single P–N bond in $H_3\overline{N}PO_3^2{}^-Na^+$ (1.77 Å).[94] The angles are the same in both molecules: ∠N–P–N = 82.5° and ∠P–N–P = 97.5°.

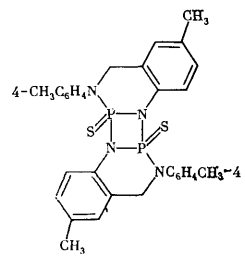
The results of X-ray diffraction studies on several diazadiphosphetidine dioxides and disulphides are presented in Table 3. It is noteworthy that the P...P and N...N distances in diazadiphosphetidine molecules are in the ranges 2.48–2.562 Å and 2.22–2.26 Å, which is less than the sum of the van der Waals radii (3.60 and 3.10 Å). These data indicate the occurrence of the transannular P...P and N...N interaction[95]. The stronger P...P repulsion explains the acute angle at the phosphorus atoms[96].

Table 3. The bond lengths and angles in 1,3,2λ^3,4λ^3-diazadiphosphetidines and 1,3,2λ^5,4λ^5-diazadiphosphetidine 4-oxides and 4-sulphides.

Formula	P–N bond length, Å	Angle, °		Refs.
		N–P–N	P–N–P	
{ClP–NC$_4$H$_9$-t)$_2$* (*cis*)	1.689	82.5	97.3	[92]
([CH$_3$)$_3$Si]$_2$NP–NSi(CH$_3$)$_3$)$_2$ (*trans*)	1.727	82.5	97.5	[33]
{ClP(O)–NC$_4$H$_9$-*trans*)$_2$**	1.661	85.5	94	[98]
(C$_6$H$_5$P(S)–NC$_2$H$_5$)$_2$** (*trans*)	1.688	83.25	96.25	[96]
{C$_6$H$_5$P(S)–NC$_2$H$_5$)$_2$* (*cis*)	1.687	84.2	95.2	[99]
(C$_6$H$_5$P(S)–NC$_2$H$_5$)$_2$** (*trans*)	1.686	83.4	96.7	[99]
(C$_6$H$_5$P(S)–NCH$_3$)$_2$**	1.69	84.0	96.0	[45]
(C$_6$H$_5$P(S)–NC$_6$H$_5$)$_2$**	1.695	81.9	98.1	[45]
(ClP(S)–NCH$_3$)$_2$**	1.67	84	96	[100]

*Non-planar ring.
**Planar ring.

In a polycyclic molecule the P–N bond lengths in the diazadiphosphetidine fragment are unusually large and nonidentical, although the ring is planar and the P–N–P (91°) and N–P–N (89°) angles approach the right angle[97]:



In the molecules of diazadiphosphetidine with phosphorus(V) one P–N bond is axial and the other is equatorial[11].

The results of the determination of the bond lengths and angles in 1,3,2λ^5,4λ^5-diazadiphosphetidines obtained by different investigators are listed in Table 4.

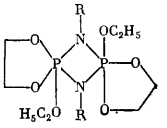
The molecule of *trans*-2,4-diethoxy-2,4-bis(ethylenedioxy)-1,3-di-*p*-tolyl-1,3,2λ^5,4λ^5-diazadiphosphetidine has a centrosymmetric structure and the mutual orientation of

the dioxaphospholan ring and the central four-membered nitrogen-phosphorus ring corresponds to the *trans*-configuration. Two nitrogen–phosphorus bonds occupy axial and equatorial positions in the trigonal bipyramid at the phosphorus atom. The dioxaphospholan ring also has the axial-equatorial configuration, i.e., of the two ring bonds, one P–O bond is axial (1.678 Å) and the other is equatorial (1.635 Å). For the axial-equatorial arrangement of the rings, the existence of the *cis*-isomer becomes impossible.

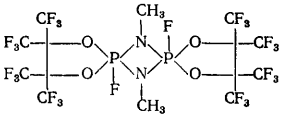
Table 4. The bond lengths and angles in planar $1,3,2\lambda^5,4\lambda^5$-diazadiphosphetidines.

Formula	P–N bond length, Å		Angle, °		Refs.
	axial	equatorial	N–P–N	P–N–P	
$[(CCl_3)F_2P{-}NCH_3]_2$	1.742	1.621	79.9	100.1	[61,94]
$(F_3P{-}NCH_3)_2$	1.735	1.595	77.2	102.9	[105]
$[(C_6H_5)F_2P{-}NCH_3]_2$	1.750	1.631	79.8	100.2	[105]
$[(C_6H_5)F_2P{-}NCH_3]_2$	1.78	1.64	80.6	99.4	[107]
$[(C_6H_5)_2FP{-}NCH_3]_2$	1.779	1.654	78.6	101.8	[108]

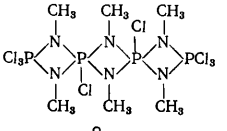
The geometrical characteristics of the diazadiphosphetidine ring are as follows: axial P–N bond length 1.785 Å, equatorial P–N bond length 1.652 Å, ∠N–P–N = 79.7°, and ∠P–N–P = 100.3°; the ring is ideally planar[101]:



Similar data were obtained for tricyclic dispirodiazadiphosphetidines:

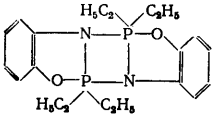


(axial P–N bond length 1.787 Å, equatorial P–N bond length 1.626 Å, ∠N–P–N = 84.1°, and ∠P–N–P = 95.9° [102]) and



(axial P–N bond length 1.75 Å and equatorial P–N bond length 1.64 Å [103]).

The bicyclic phosphabenzoxazole system in the molecule of the dimeric 2,2-diethyl-2-phosphabenzoxazole is planar and forms a dihedral angle of 1.2° with the plane of the four-membered ring. The axial and equatorial P–N bond lengths (1.812 and 1.681 Å) are close to those obtained for other $1,3,2\lambda^5,4\lambda^5$-diazadiphosphetidines, while the N–P–N valence angle is reduced and the P–N–P angle is increased by 4–5°. This finding as well as the appreciable distortion of the trigonal-bipyramidal coordination of the phosphorus atom can be explained by the fact that it is included in two rigid planar rings—the diazadiphosphetidine and oxazaphosphole rings[104]:



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Advances in the Study of *s-cis-trans*-Isomerism—Stereochemistry of Carbonyl Derivatives of Five-membered Heterocycles

V.N.Sheinker, A.D.Garnovskii, and O.A.Osipov

Results obtained on the stereochemistry of carbonyl derivatives of five-membered heteroaromatic systems—furan, thiophen, selenophen, tellurophen, pyrrole, and azoles—are summarised and systematised. Factors responsible for the stereochemical behaviour of conformationally non-rigid *s-cis-trans*-isomers of carbonyl derivatives of five-membered hetaryls are isolated. A list of 287 references is included.

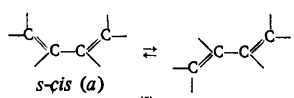
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I. INTRODUCTION

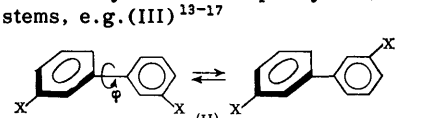
An important problem in the present-day stereochemistry of organic compounds is *s-cis-trans*-isomerism[1-3], involving the appearance of conformationally non-equivalent structures as a result of restricted rotation of molecular fragments about a single bond situated between two multiple bonds. The conjugation of double bonds through a single bond raises the energy barrier to rotation about the latter and increases significantly the latter's double-bonded character (the situation is analogous to *cis-trans*-isomerism, which is the reason for the fundamental similarity in the terms used for the isomers).

The phenomenon of *s-cis-trans*-isomerism, discovered[4] in butadiene systems

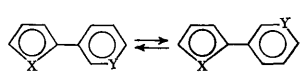


s-cis (*a*) (I) *s-trans* (*b*)

has proved to be widespread in aliphatic[1,2,5], aromatic[1,6-10], and heterocyclic[3,11-18] systems. Both planar structures, characterised by maximum conjugation, can be realised in butadiene and other aliphatic systems of type (I).[19] With conjugated aromatic systems like biphenyl (II)[6,7] and heteroaromatic systems, e.g. (III)[13-17]



X,X-*cis* ($0° < \varphi < 90°$) (II) X,X-*trans* ($180° < \varphi < 270°$)

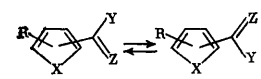


X,Y-*cis* (III) X,Y-*trans*

steric hindrance gives rise to non-planar structures corresponding to the optimum balance between conjugation and repulsion interactions. Unsymmetrical structures (II) and (III) may also give rise to *s-cis-trans*-isomerism. Finally, this can occur also in systems in which an aromatic or a heteroaromatic ring is conjugated with an unsaturated acyclic fragment, e.g. C=Z, where Z = C<, O, S, Se, N−, P<−†.

† Henceforward we shall arbitrarily apply the term "conformationally mobile" to such fragments.

This type of isomerism arises in aromatic systems only on the introduction of a second substituent into the ring (*ortho* or *meta* to the C : Z group).[3,20] With heterocycles, in contrast, introduction of a single conformationally mobile group is sufficient for the appearance of two isomers (IV), owing to diminution in the symmetry of the molecule to C_s and C_1:



X,Z-*cis* (IV) X,Z-*trans*

Among isomers of C : Z-containing heterocycles a most important place is occupied by carbonyl-containing derivatives (IV: Z = O), which have been investigated intensively by almost all current physical, physicochemical, and quantum-chemical methods (>80% of all the papers considered in the present Review have been published during the past decade).

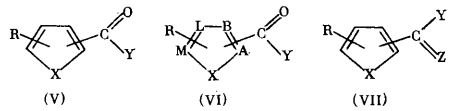
The reason for such heightened interest in the stereochemistry of carbonyl derivatives of five-membered heteroaromatic systems is that they form a convenient model for establishing general laws and elucidating the factors that explain various aspects of *s-cis-trans*-isomerism. Furthermore, knowledge of conformational transitions in such systems is necessary to establish the mechanism of several chemical[21] and photochemical[22] processes, and also to explain the biological action of preparations based on them[23,24]. Carbonylfurans have been used as internal and external standards in dynamic carbon-13 nuclear magnetic resonance spectroscopy for accurate temperature measurement[25].

However paradoxical it may appear, this particular type of isomerism has been inadequately discussed in well known monographs[2,5,6,8,26-28].# Yet progress in the study of *s-cis-trans*-isomerism and the huge quantity of publications make a review of this topic necessary.

The present Review gives a critical analysis of results on the *s-cis-trans*-isomerism of carbonyl-substituted five-membered heteroaromatic systems—furan, thiophen, selenophen, tellurophen, and pyrrole (Va-e), azoles (VI) and their

This problem is raised in certain reviews[3,5,18,29-32].

arylated derivatives—as well as structural analogues of carbonyl compounds (VII)



(V) (VI) (VII)

(V)–VII): (a) X = O; (b) X = S; (c) X = Se; (d) X = Te;
(e) X = NR′ (where R′ = H, Alk, Ar);
R = n-Alk, Ar, cyclo-C_4H_4, NO_2, Hal, CO.Y;
Y = H, Alk, Ar, Het, OH, OR″ (where R″ = Alk, Ar), Cl, NH_2;
(VI): A, B, L, M = N;
(VII): Z = CH.R″′ (where R″′ = H, Alk, Ar, Het), N.OH, N.Ar.

Attention is paid to the influence of the nature of the heterocycle, the character and the position of the conformationally mobile group and the substituent R in the heterocycle, the medium, and complex formation on the stereochemistry of systems of types (V)–(VII).

II. METHODS OF INVESTIGATION OF *s-cis–trans*-CONFORMERS

Vibrational Spectroscopy

In many cases analysis of vibrational spectra is an extremely effective method for establishing the presence of a conformational equilibrium[2,6,7,32-34]. It is usually assumed in such investigations that the normal vibration frequencies of the conformers differ somewhat owing to kinematic or dynamic factors. On such a hypothesis the main criteria of the presence of a mixture of conformers in liquids, solutions, or gases are complication of the spectra, variation in relative band intensities with temperature and solvent polarity, and simplification of the spectrum ("freezing" of the bands) in the liquid–crystal transition[6,34].

In the infrared, *s-cis–trans*-isomerism in carbonyl derivatives (V) and (VI) is usually indicated by a carbonyl absorption doublet ν_{CO} in the range 1660–1790 cm^{-1}. However, the nature of this doublet has been a matter of controversy. For 2-furaldehyde and 2-formylpyrrole it is explained by the presence of *s-cis–trans*-isomers[35-43], Fermi resonance[44-48], and also molecular association[42-51]. The doublet in the infrared spectrum of 2-formylthiophen is attributed mainly to Fermi resonance[52-54], although other workers[41] ascribe it to conformational equilibrium.

Thus existing data do not permit unambiguous interpretation of the behaviour of ν_{CO} nor definite conclusions on the conformations of carbonyl derivatives of five-membered heterocycles. Theoretical analysis of vibrational spectra[45, 48,55,56] has helped to explain the differences in the spectra of conformers and to give a more profound interpretation of the modes of vibration of each. Calculation has shown[56] that the doublet in the range 1670–1710 cm^{-1} is indeed due to the presence of both conformers, the ν_{CO} vibration being composite: the position of the carbonyl group affects not only the 1680- and 1700-cm^{-1} vibrations (X,O-*cis* and X,O-*trans*) but also the absorption at 1570 cm^{-1}, which is due to a fragment of the heterocycle ($\nu_{C(2):C(3)}$).

Frequency assignments for furaldehyde in other infrared regions, also used[40] for the study of *s-cis–trans*-isomerism, have been refined[55,56]. The integral absorption band intensities necessary to determine the state of conformational equilibrium were found[55,56]. The ratio of the conformers cannot[55] be evaluated solely from the experimental intensity ratio of ν_{CO} bands in the infrared spectra of furaldehyde.

The above discussion shows that, although infrared spectral data can be used to assess *s-cis–trans*-isomerism in a series of carbonyl derivatives of five-membered heteroaromatic systems, reliable results can be obtained only by combining empirical and calculated values for the vibrational spectra.

Dielectric and Electro-optical Investigations

Several dielectric and electro-optical investigations have been made on conformational equilibrium in the above systems. However, even in this case the solution depends on the choice of additive scheme, so that the use of group moments for aromatic substituents may not always be successful[57-59].

In connection with this the dipole moment of the aldehyde group was determined[60] for compounds of the furan series on the assumption that furaldehyde exists only in the O,O-*cis*-form. Dipole moments have been calculated theoretically[61-63] for both isomers of a series of aldehydes.

The controversial aspect of the vector calculation of dipole moments for heterocyclic aldehydes is to allow for the moment of interaction between heteroatom and carbonyl oxygen, first introduced for furaldehyde[64]. Values from 0 to 0.3 D have been assigned to this quantity[65-67].

A contradictory explanation has been given for dielectric results for carbonyl derivatives of thiophen (V: X = S, Y = R = H)[68], selenophen (V: X = Se, Y = R = H)[59,69,70], tellurophen (V: X = Te, Y = R = H)[71], and benzimidazole (VI: X = NAlk, A = L = M = CH, B = N, R = cyclo-C_4H_4).

Application of the Kerr effect has also led to opposite conclusions[58,68] concerning the preferential conformation of furaldehyde. These discrepancies are due both to difference in the valency–optical scheme used and to disagreement in the experimental results.

In several cases the above contradictions are due mainly to incorrect choice of vector additive and valency–optical schemes for the theoretical calculation of dipole moments and anisotropy of polarisability of the molecules of carbonyl derivatives of five-membered heteroaromatic systems. Therefore a definite advance in the use of dielectric measurements and the Kerr effect to assess the *s-cis–trans*-isomerism of these systems was determination of the polarisability tensors for several fundamental heterocycles[74-76] and the construction of valency–optical and vector–additive dipole schemes for calculating azole molecules[77-79]. Finding the formyl group moments for 2-furaldehyde and 2-formylthiophen from independent data was of great value[80,81].

Thus the limitations of the dielectric and electro-optical methods are inherent in their very foundations, in the problem of choosing adequate group moments and polarisability tensors. Since a correct solution of such a problem is often difficult or even impossible, the results may not agree and may differ from those obtained by other methods. However, with a right choice of these quantities a simultaneous application of the methods may be extremely fruitful for solving problems of conformational analysis.

Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy has recently become one of the most widely used methods for investigating *s-cis–trans*-isomerism. It was first shown[82] that the conformations of 2-formyl derivatives of five-membered heterocycles can be assessed from the stereospecific spin–spin coupling constants in the ^1H n.m.r. spectra. It was later

found possible[83] to determine the position of the *s-cis–trans*-isomeric equilibrium and its thermodynamic parameters from such spectra. Unfortunately, errors were made in the detailed investigations[83], which led to a wrong conclusion on the ratio of the stable conformers. Nuclear magnetic resonance (^{1}H), together with stereospecific constants, chemical shifts, the Overhauser effect, and shift reagents, has been used to investigate the structure of carbonyl derivatives of furan[36,55,82–89], thiophen[85,88–96], selenophen[84,89], pyrrole[97,98], tellurophen[71,95,99], and azoles[100–104]. Isolated results have appeared on the application of carbon-13 and fluorine-19 n.m.r. in the conformational analysis of carbonyl derivatives of five-membered heterocycles[105–107]. However, the possibilities of n.m.r. spectroscopy are also limited, since its use presupposes either the availability of stereospecific hyperfine coupling constants, adoption of a definite model of diamagnetic shielding, or measurements at temperatures below the coalescence point. The postulates necessary also in application of the Overhauser effect and shift reagents restrict the use of these methods. The work is greatly complicated by increase in the order of the n.m.r. spectrum and sparing solubility of the compound. Nevertheless, n.m.r. spectroscopy is one of the most promising methods of investigation in the conformational analysis of *s-cis–trans*-isomers.

Use of electron spin resonance spectroscopy becomes possible for heterocyclic aldehydes only when they generate radical-anions[12,108,109]. The range of such compounds is limited, and the position of conformational equilibrium in the radical system differs from that for the neutral molecule.

The conformations of carbonyl derivatives of five-membered heterocycles have been analysed not only by the above main methods of investigation but also on the basis of data of microwave spectroscopy[110–113] (in the gas phase), ultrasonic[114] and dielectric[103,115] relaxation, X-ray examination[116–120] (of the crystalline phase), and electronic spectra[121–124].

Quantum-chemical Methods

The *s-cis–trans*-conformations of carbonyl derivatives of five-membered heterocycles (mainly aldehydes) have been widely assessed by quantum-chemical methods. Furaldehyde[5,62,63,123,125–129] has been investigated in the greatest detail by the Pariser–Parr–Pople, INDO/2, and extended Hückel methods, although the conclusions concerning realisation of a particular conformer obtained from the calculations are contradictory. A similar situation obtains in the assessment from quantum-chemical calculations of conformers of formylpyrrole[63,123] and formylthiophen[93,130,131].

Such a discrepancy in the conclusions concerning the configurations of carbonyl derivatives of five-membered heterocycles can be explained by the very small energy difference between the two conformers, hundredths of an electron-volt; i.e. the result may change depending on the approximations and the method of calculation. The role of *d*-orbitals in calculations on the conformations of the 2-formyl-thiophen and -selenophen is equally debatable[93,123,130].

Application of the comparatively simple extended Hückel method of calculation[132,133] led to important conclusions also on *s-cis–trans*-isomerism and barriers to internal rotation in heteroaromatic aldehydes[134,135].

The results in the present section can be summarised by emphasising the inconsistency of individual conclusions reached by different physicochemical methods on the conformations of carbonyl derivatives of five-membered heterocycles. Therefore only those results are reliable that coincide for different methods and produce a single, internally consistent picture in series of compounds with variation in heterocycles, substituents, and conformationally mobile groups.

III. FACTORS INFLUENCING THE POSITION OF CONFORMATIONAL EQUILIBRIUM§

Among factors responsible for the conformation of carbonyl-substituted five-membered heterocycles we have isolated the structure of the hetero-system with the exocyclic substituent, the medium, and intra- and inter-molecular interactions.

1. Structure of *C*-Carbonyl-substituted Heterocycles

(a) Substituents Attached to the Carbonyl Group (COR)

Aldehydes (R = H). No generally accepted view can be found on the most stable conformers of the simplest 2-formyl derivatives of five-membered heterocycles: the position of conformational equilibrium determined by different methods even under closely similar conditions often varies so widely that all the data available are insufficient to determine which form is the most stable and predominant.

The situation is especially characteristic of 2-furaldehyde: whereas it has been stated[42,64,83] that the O,O-*trans*-form is energetically the most advantageous, other workers[85,88,95,106,136,137] regard the O,O-*cis*-conformer as the most stable. More unambiguous conclusions have been reached on the structure of 2-formylthiophen, which most investigators[85,88,90–96,110,111,138–142] regard as existing solely in the form of the S,O-*cis*-conformer. Yet the agreement between experimental and calculated dipole moments led to the conclusion[140] that thiophen-2-aldehyde exists as a non-planar S,O-cisoid structure with a non-coplanarity angle of 35°, and other workers[68] assume the existence of an equilibrium mixture of conformers containing up to 27% of the S,O-*trans*-form.

2-Formylselenophen is regarded[59,70,84] as conformationally a more rigid system than 2-formylthiophen. The Se,O-*cis*-isomer is the more stable[59,69,70,95,143], although the conformational mixture may contain a considerable percentage of the *trans*-form[84,143].

Nuclear magnetic resonance and infrared spectroscopy[99], and also dipole moments[59,144], suggest that 2-formyltellurophen exists in solution as a mixture of two conformers, with a lower content of the *trans*-form than in the case of furaldehyde. However, even with this aldehyde shift reagents reveal exclusively the Te,O-*cis*-conformer[95]. Thus, despite appreciable discrepancies in the results, the X,O-*cis*-conformers are the most stable in 2-formylhetaryls containing

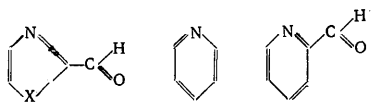
§ In most cases the solvents in which investigations have been made are not stated in the present Review if change in them does not lead to fundamentally different results. The solvents mainly used in the work cited were as follows: tetrachloromethane, benzene, and dioxan in dielectric measurements; tetrachloromethane, chloroform, dichloromethane, dioxan, and mineral oil in infrared spectroscopy; and tetrachloroethylene, chloroform, methanol, dichloromethane, tetrachloromethane, and acetonitrile in radiospectroscopy.

elements of subgroup VI*b* as heteroatom¶, the content of this form diminishing in the sequence—selenophen > thiophen > tellurophen > furan.

The authors of the majority of the investigations consider[49-51,97,103,115,145-148] that pyrrole-2-aldehyde exists as the N,O-*cis*-conformer. Yet other results[83,98,103,115,145,149,150] indicate a definite contribution by the N,O-*trans*-form, though this can be explained[151] also by the possible existence of a non-planar conformer of 2-formylpyrrole. Stabilisation of the N,O-*cis*-conformers in this compound was originally explained[146] by a hydrogen bond of the type NH...O=C. Later, however, it appeared[98,152,153] that no significant increase† in the proportion of the N,O-*trans*-conformer occurs even in *N*-alkyl derivatives of this aldehyde. The N,O-*cis*-form is characteristic also of 2-formylindole[155].

Thus the factors causing stabilisation of the X,O-*cis*-conformers of the 2-formyl derivatives are common to all the five-membered heterocycles considered, and hence independent of the nature of the heteroatom X. A decisive role is played by Coulombic interaction of the charges of the cyclic heteroatom and the carbonyl oxygen atom. ππ-Conjugation of exo- and endo-cyclic parts of the molecules is not decisive (in the presence of Coulombic interactions), and can merely be superposed on the predominant Coulombic effect, either strengthening or weakening it. For these aldehydes both effects give the X,O-*cis*-forms[156-158].

2-Aldehydes of the azole series are characterised[159,160] mainly by conformationally rigid *cis*-structures (VIII)#. To understand the factors stabilising the *cis*-configuration of the 2-formylazole systems it must be borne in mind that molecules of aldehydes of the 1,3-diazole series (VIII) include fragments of the fundamental five-membered heterocycles (V) and six-membered nitrogenous heteroaromatic systems [azines, in particular pyridine (IX)]. Examination of the structure 2-formylpyridine[11,43,63,82,113,123,161-169] indicates almost complete formation§ of the rigidly fixed N,O-*trans*-isomer (X)



(VIII) (IX) (X)

¶ However, other studies[83,145] suggest that the X,O-*trans*-conformer predominates in the 2-aldehydes of furan and pyrrole.

† It must be emphasised, however, that the presence of significant steric hindrance (in *N*-aryl- and *N*-hetaryl-2-aldehydes)[154] leads to the O,N-*trans*-structure, in which Coulombic repulsion is minimal.

To avoid confusion we retain for the carbonylazole systems (VIII) the names of conformers analogous to the formyl derivatives of the fundamental five-membered heterocycles.

§ Yet other workers[82,165,170] regard pyridine-2-aldehyde as a stereochemically non-rigid system with up to 30% of the N,O-*cis*-form involved in the conformational equilibrium. This is well explained by both the above factors responsible for stabilising conformers in the *s-cis*–*trans*-equilibrium of formyl-containing heterocycles.

Indeed, both Coulombic interaction (repulsion of negatively charged nitrogen and oxygen atoms) and ππ-conjugation effects stabilise the planar N,O-*trans* form of pyridine-2-aldehyde (X). The above results suggest that both effects should tend to stabilise the X,O-*cis*(N,O-*trans*)-conformers (VIII) in the case of 2-formylazole systems, as has been confirmed experimentally[73,159,160] and by calculation[159].

In this connection the conclusion[72] that up to 50% of the X,O-*trans*-isomer of 2-formyl-*N*-methylimidazole is present in benzene solution appears unexpected, though it is difficult to deny the actual possibility that the X,O-*trans*-isomeric form may be involved in the conformational equilibrium of aldehydes of the azole series[73,160].

Ketones (R = Alk, Ar, Het). The attachment of aliphatic, aromatic, and heterocyclic substituents to the carbonyl group changes the barrier to rotation about the single bond

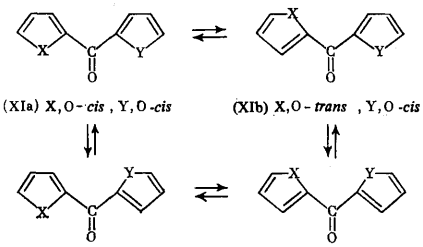


and in most cases leads to structural non-coplanarity of ketone derivatives of five-membered heterocycles[134,154,171]. Even the simplest alkyl substituent, methyl, yields two isomers, with the O,O-*trans*-form predominating in 2-acetylfuran[42,68,93,94,136,137,171-174]. Yet 2-acetylthiophen, 2-acetylselenophen, and 2-acetylpyrrole are characterised exclusively or predominantly by the planar X,O-*cis*-structure[69,92,103,124,140,152,175-178]. However, some data even for these compounds indicate both the establishment of a conformational equilibrium[59,68,94,152] and the presence of a substantially non-planar structure[152,178,179] with a dihedral angle $\phi \cong 30-55°$. Increase in the proportion of the *trans*-conformer (from 28% to 53%) is observed on passing from formyl to acetyl derivatives of tellurophen[59,99,144]. The inconsistency of all these results on the three-dimensional structure of the acetyls is due to the difficulty usually encountered in choosing unambiguously, on the basis of individual data, between non-planar rotamers and equilibrium systems containing planar *s-cis*- and *s-trans*-conformers.

A non-planar structure is characteristic of hetaryl phenyl and dihetaryl ketones[178,180,181]. That of furyl phenyl ketone is due solely to displacement of the phenyl group from the plane of the rest of the molecule[180], whereas the corresponding thienyl ketones exhibit simultaneous displacement of the hetaryl group from the plane of the carbonyl group[181]. This result is due to the greater gain in energy on conjugation of the carbonyl with the less aromatic[182] furan ring than with the thiophen ring, as is confirmed by quantum-chemical calculation[123].

Thus the conformational analysis of ketones, in contrast to that of aldehydes, must take into account not only *s-cis*(*trans*)-conformers but also the possibility of a non-planar molecular structure for the carbonyl-containing five-membered heteroaromatic systems[23,67,68,92,121,124,183-186]. Like the corresponding aldehydes, ketones of azoles usually have predominantly a structure with maximum separation of pyridine-type nitrogen atoms and carbonyl oxygen[187,188]. Addition of two heterocycles to a carbonyl group usually complicates the task of conformational analysis, since the possibility arises

of four planar conformers (XIa–d):



(XIa) X,O-*cis*, Y,O-*cis* (XIb) X,O-*trans*, Y,O-*cis*

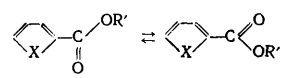
(XIc) X,O-*cis*, Y,O-*trans* (XId) X,O-*trans*, Y,O-*trans*

A non-planar structure is also possible for the ketones, as a consequence of electronic and steric effects of interaction between the heterocyclic rings and with the carbonyl group.

According to n.m.r. data difuryl ketone probably exists as a mixture of equal quantities of two forms, O,O-*cis*,O,O-*trans* and O,O-*trans*,O,O-*trans*[185]. Infrared[189] and n.m.r.[185] spectroscopy lead to fundamentally opposite conclusions on the structure of fur-2-yl fur-3-yl ketone. Whereas changes in dipole moments could not give an unambiguous indication of the spatial structure of dithienyl ketone[67], application of this method together with the Kerr effect has shown[68,181] a non-coplanar *cis,cis*-structure with the thienyl diverging from the carbonyl plane by 30–55°. Dielectric measurements and n.m.r. spectroscopy have demonstrated an unsymmetrical planar structure for a series of thioketones of pyrazole, thiophen, and several other heterocycles[190].

Carboxylic acids (R = OH). In contrast to aldehydes and ketones, *s-cis–trans*-isomerism in carboxylic acids of five-membered heterocycles has remained almost uninvestigated. X-Ray structural studies indicate that thiophen-, selenophen-, and tellurophen-carboxylic acids exist in the crystalline phase as planar X,O-*trans*-configurations, whereas furancarboxylic acid is characterised by the O,O-*cis*-form[119]. 1,3-Dimethylpyrazole-5-carboxylic acid has a planar N,O-*trans*-structure in the solid state[118].

Carboxylic esters (R = OR'). The esters have been investigated in greater detail. It can be accepted that the *s-cis–trans* equilibrium



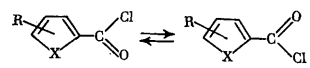
(XIIa) X, O_{carb}-*cis* (XIIb) X, O_{carb}-*trans*

is established in solution[47,59,65,106,191–193], but the clear dependence on the nature of the heterocycle characteristic of aldehydes is not observed[59]. Furancarboxylic esters (XII: X = O, R' = H) exist mainly as the X,O-*trans*-form (XIIb), which according to dipole moments[65] and n.m.r. spectra[106] constitutes 50–70%. Increase in the degree of branching of the group R' entails lowering of the barrier to rotation, which makes the identification of conformers difficult[106]. The content of the *cis*-conformer in conformational equilibrium is according to the dipole moments respectively 33%, 59%, and 42% in thiophen-, selenophen-, and tellurophen-carboxylic esters, in contrast to aldehydes and ketones.

These quantitative relations can hardly be regarded as sufficiently accurate, since it has been reported that conformational processes in thiophen- and furan-2-carboxylic acids have similar enthalpies, and also that furan- and tellurophen-carboxylic esters have equal contents of the two conformers[191].

In contrast to the above esters, methyl pyrrole-2-carboxylate exists in solution predominantly (73%) in the planar N,O_{CO}-*cis*-form: the rather higher content of the N,O-*trans*-isomer than in aldehydes and ketones is attributed to the ability of the imino-group to form a hydrogen bond not only with the carbonyl but also with the ethereal oxygen of the carboxyl group[194].

Acid halides (R = Hal). The barrier to rotation is higher in the chlorides of carboxylic acids of five-membered heterocycles than in the hetaryl methyl ketones, with a consequent conformational equilibrium between two planar conformations:



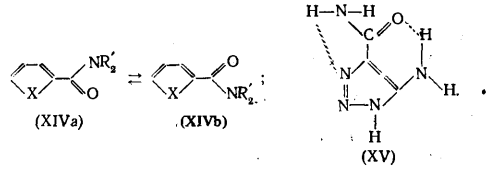
(XIIIa) (XIIIb)

Data on the conformations of acid halides are restricted to furan and thiophen derivatives[47,65,105,106,195,196].

According to ^{1}H n.m.r. spectra[106] the equilibrium mixture of molecules of the chloride of furancarboxylic acid contains at low temperatures (~193 K) up to 90% of the O,O-*cis*-form (XIIIa). The same form (XIIIa) is predominant also in chlorides of thiophencarboxylic acids[195,197], although infrared spectra suggest[105] a significant contribution by the S,O-*trans*-form (XIIIb). The sequence is reversed on passing from chlorine to fluorine derivatives, and the proportion of the X,O-*cis*-form diminishes: under comparable conditions (solvent, temperature) the proportion of the O,O-*cis*-conformer of the fluoride of furancarboxylic acid is 75%, but in the corresponding thiophen derivative it has even dropped to 55%. This is obviously due to the strongly electronegative fluorine substituent, which is able to compete with the carbonyl oxygen in its ability to interact electrostatically with the endocyclic sulphur atom ($S^{\delta+}...F^{\delta-}$ and $S^{\delta+}...O^{\delta-}$), and this leads to approximate equivalence of the two forms in the thiophen derivative. In fluorides of furancarboxylic acids, on the other hand, the Coulombic repulsion between the terminal oxygen and the fluorine atom exceeds that between the two oxygen atoms, so that the proportion of the O,O-*cis*-form in them is higher[105] than in the corresponding aldehydes of the furan series.

Similar conclusions on the competitive electrostatic interaction of halogen and carbonyl oxygen with the cyclic heteroatom were reached in an investigation of conformational changes in series of chlorides of furan-2-carboxylic acids[196]. A detailed investigation showed, on the basis of infrared spectral data together with measurements of dipole moments and the Kerr effect, that such chlorides are present in solution as mixtures of two conformers, the proportion of the O,O-*trans*-form increasing with the acceptor properties of 5-substituents in the furan ring and with decrease in solvent polarity, whereas chlorides of thiophencarboxylic acids are characterised by a single O,S-*cis*-conformation (XIIIa).

Amides of carboxylic acids (R = NH_2, $NAlk_2$). In amides of carboxylic acids of five-membered heterocycles the barrier to rotation is much lower than in the aldehydes, which leads to predominance of a non-planar X,O-*trans*-structure (XIVb)[94,95,171]:



(XIVa) (XIVb) (XV)

Measurements of dipole moments indicate[59] that the 2-dimethylcarbamoyl derivatives contain in the equilibrium mixture respectively 89% (furan, tellurophen), 67% (selenophen), and 44% (thiophen) of the X,O-*trans*-isomers.

Whereas the non-planar structure of these compounds is apparently due to steric effects, formation of a predominantly X,O-*trans*-structure is a consequence of X...N and X...O electrostatic interactions[95]. Crystallographic examination[198] of 5-amino-1,2,3-triazole-4-carboxamide reveals in the solid state a structure of *trans*-type stabilised by fairly strong intramolecular hydrogen bonds. Furthermore, such an $N_{(3)}$,O-*trans*-conformation is consistent with the principle of maximum distance between a negatively charged oxygen atom and the pyridine nitrogen atom of the heterocycle.

The carbothioamides possess a considerably lower energy barrier (2.4–4.4 kcal mole^{-1})[199] than the 2-carboxamides of five-membered heterocycles and pyridine, but this hinders free rotation of the thiocarbamoyl group. Dielectric measurements show that furan-2-carbothioamide exists in benzene solution as a mixture of both planar conformers in the approximate proportions 2 : 1 (excess of the S,O-*trans*-form). On the other hand, the thiophen analogue is characterised by a fivefold excess of the S,S-*cis*-conformer. On the whole these results are consistent with what is known for the corresponding formyl and carbamoyl derivatives. However, the low energy barriers and the small difference in energy of the two forms (0.2 kcal mole^{-1}) facilitate appearance of the S,S-*trans*-form in thiophen-2-carbothioamide[199].

We note in conclusion that in none of the above carboxamide and carbothioamide derivatives could the coalescence point be reached (according to the ^{1}H n.m.r. spectra). This is due either to realisation of a single form (X,O-*trans*) or (more probably) to a low barrier to rotation (below 5–6 kcal mole^{-1}).[200]

Comparison of the structures of the various derivatives of carboxylic acids of five-membered heterocycles must take into account the great influence of the nature of the conformationally mobile group on the position of the conformational equilibrium. Compounds containing alkoxycarbonyl and dialkylcarbamoyl groups exhibit a shift in the equilibrium towards the X,O-*trans*-form. This is especially marked in carboxamides, with almost complete reversal of the equilibrium accompanied by a considerable lowering of the barrier to rotation and appearance of the ability to form non-planar structures. The situation is quite different with acid halides, where the state of the conformational equilibrium is determined by the halogen atom and its ability to compete with the carbonyl oxygen in attracting or repelling the heteroatom of the aromatic ring. This explains the marked difference in conformational equilibrium between acid chlorides and acid fluorides.

(b) Position of the Carbonyl Group in the Heterocycle

The remoteness of the carbonyl oxygen atom from the oppositely charged endocyclic atom X in 3-carbonyl derivatives facilitates the production of *s-trans*-conformations, which in individual cases may become the predominant or even sole form. This conclusion is confirmed theoretically for many 3-aldehydes[123,201]. Experimentally n.m.r. spectroscopy indicates[202–204] that the proportion of the *s-trans*-form in the 3-aldehydes of pyrrole, thiophen, and furan is respectively 78%, 82%, and 100%. Only introduction of a bulky (e.g. ester) substituent at position 2 in the heterocycle is able to change slightly the proportions of the conformers[203]. The structure of the latter has been confirmed by infrared spectroscopy[189] and by dielectric measurements[66,141,173,205].

The differences in the behaviour of 3-substituted furan and thiophen derivatives are explained[203] by the net effect of Coulombic (X...O_{ald}), dipole–dipole ($C_{(2)}$=$C_{(3)}$ and O=C), and resonance interactions. These three factors, acting in the same direction, lead to exclusive formation of the O,O-*trans*-modification in 3-formylfuran, but to both planar forms, with the S,O-*trans*-conformer predominating, in the thiophen analogue. Investigation of the conformations of the 3-formylselenophen gives more contradictory results. Thus the dipole moments indicate[143] that in benzene solution this aldehyde contains both conformers, in roughly equal quantities with the Se,O-*cis*-form in slight excess, whereas other dielectric measurements and proton n.m.r. spectroscopy suggest that the content of the Se,O-*cis*-form does not exceed 20%.[70,99]

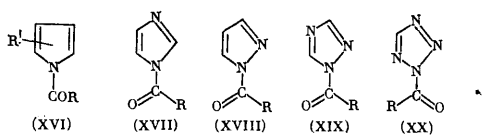
In the case of pyrrole-3-aldehyde the planar N,O-*trans*-structure is the most highly populated[97,115,206,207] and apparently[147] the only form. Substituents and solvents are able merely to disturb the ratio of the conformers, but not to change the general tendency. Pyrazole-4-aldehyde, in which the formyl group is arranged approximately as in the previous compound, exists according to the ^{1}H n.m.r. spectra as an equilibrium mixture of N,O-*cis*- and N,O-*trans*-isomers[208]. The activation energy of isomerisation is smaller by 1.5 kcal mole^{-1} than for the corresponding pyrrole-3-aldehyde[208].

The content of the more stable X,O-*trans*-form in the 3-acetyl derivatives of five-membered heterocycles increases in the same sequence—from *N*-methylpyrrole through thiophen to furan—as for their formyl analogues[202]. However, the proportion of the conformers is less displaced towards this form than in the case of aldehydes: according to n.m.r. spectral results obtained by the use of shift reagents of the Overhauser nuclear effect[202] its content is on the average 52%, 56%, and 70% respectively (in the aldehydes 78%, 82%, and 97%). When the temperature is lowered to −100 °C coalescence of the signals cannot be observed in either 3-acetylfuran or 3-acetylthiophen, which indicates a low barrier to rotation in these compounds and less conjugation in 3- than in 2-substituted derivatives[185]. As in other five-membered heterocycles, the content of the X,O-*cis*-conformer in 3-acetylselenophen is double that in the 3-formyl analogue (30% and 15%).[99] 4-Acetylimidazole exists in the crystalline state solely in the $N_{(3)}$,O-*trans*-form[187].

Conformational equilibria in other 3-carbonyl derivatives of five-membered heterocycles (acids, esters, acid halides, and amides) remain almost uninvestigated.

2. *N*-Acyl Derivatives of Five-membered Heterocycles

In nitrogenous five-membered heterocycles derivatives are also possible in which a COR group is directly attached to the nitrogen atom—derivatives of pyrrole (XVI) and of azoles (XVII)–(XX)



(XVI) (XVII) (XVIII) (XIX) (XX)

The structure of *N*-acylazoles, though investigated by several workers[101–103,107,162,209–213], has not until recently received an unambiguous interpretation. Authors were one in accepting a planar structure[101,102,210–212,214], but attributed

to these compounds a *cis*-structure[101,102,107,212] or a *trans*-structure[215,216] on the basis of different methods of investigation, the contents of these forms varying within wide limits in papers by different authors[101-103,209,210].

In assessments of the conformations of *N*-acylazoles a detailed investigation was therefore made into their stereochemistry by measuring dipole moments, the Kerr effect[217], and n.m.r. spectra with the use of shift reagents[104]. Among the main conclusions[104,217] are that *N*-acetylimidazole (XVII) exists as a mixture of non-planar isomers (dihedral angle 21°) containing 75% of the $N_{(3)}$,O-*trans*-form and 25% of the N,O-*cis*-form, and that *N*-acetylpyrazole (XVIII) gives a mixture of almost planar conformers (10°) containing 90% of the $N_{(2)}$,O-*trans*-form (XVIII). A non-planar $N_{(2)}$,O-*trans*-form (dihedral angle $\phi = 30°$) is characteristic also of *N*-acetyl-1,2,4-triazole (XIX). In $N_{(1)}$-acetyl-1,2,3,5-tetrazole the $N_{(3)}$,O-*trans*-form (XX) is energetically advantageous.

Thus with all the *N*-acetylazoles studied the $N_{(2(3))}$,O-*trans*-form predominates significantly in solution. The energetic advantage of this form can be attributed to attainment of maximum distance between the negative charges of the acetyl oxygen atom and the nearest "pyridine" nitrogen atom of the azole ring. A nitrogen atom at position 2 in the azole ring leads to a greater content of the *trans*-form of *N*-acetylazole than when this atom is located at position 3. The apparent reason is strengthening of electrostatic repulsion as the acetyl oxygen atom approaches the cyclic nitrogen atom. The same factor leads to flattening of the $N_{(2)}$,O-*trans*-structure.

The influence on conformation of the cyclic nitrogen atom closest to the acetyl group is especially marked in *N*-acetyltriazole (XIX), since the $N_{(2)}$,O-*trans*-form observed for it is also a disadvantageous *cis*-form with respect to the $N_{(4)}$ atom.

These conclusions were confirmed by theoretical analysis of the stability of conformers of *N*-acetylazoles (energy of barrier to rotation, difference in energy of conformers, order of bonds in planar and orthogonal forms)[218]. In contrast to Otting's views[213] the results indicate that the rise in the frequency ν(CO) on passing from *N*-acetylpyrrole to *N*-acetylazoles is due not so much to a change in aromaticity of the heterocycles as to the non-planar structure of *N*-acetylazoles.

Among other *N*-carbonyl derivatives of pyrrole and azoles only the *N*-methoxycarbonyl derivative of the former and *N*-carboxamides of pyrazole and imidazole have been investigated[101].

3. Substituents in the Heterocycle

The chief effects of substituents on the state of conformational equilibrium in carbonyl derivatives of five-membered heterocycles can be divided into three types: (A) electronic effects of substituents are transmitted through the conjugated bond system of the heterocycle, with consequent changes in degree of conjugation of hetaryl with formyl group and in charges on heteroatoms and carbon atoms; (B) direct electrostatic or other specific interaction (e.g. hydrogen bonding of a substituent with a conformationally mobile group) tends to favour one of the forms; and (C) steric hindrance by a sufficiently bulky or closely adjacent substituent tends to prevent flattening of the system or causes a change in the state of conformational equilibrium. Separation of these factors is clearly a quite complicated task, which can be successfully accomplished only in isolated cases.

Type A

Interactions of the first type can be isolated only when the two cyclic substituents (conformationally mobile, e.g. formyl, and conformationally inert) are sufficiently far apart to exert no mutual influence. This occurs in 2-aldehydes of 4- and 5-substituted furans, thiophens, selenophens, and pyrroles.

A change from electron-donor to electron-acceptor substituents produces a decrease in the proportion of the X,O-*cis*-form[42,67,219-221]. This is especially characteristic of conformationally mobile ring-substituted 2-furaldehydes. Thus for 5-substituted 2-furaldehydes the proportion of *cis*-conformer decreases from 90% to 30% in the sequence from dimethylamino through halogeno, methyl, and hydrogen to nitro[219,221]. Introduction of a 5-nitro-group leads to accumulation of the X,O-*trans*-form even in formyl derivatives of thiophen[80,135], selenophen[69,75,135], and pyrrole[23,97,147,194]. It changes the position of the conformational equilibrium in pyrrole-3-aldehyde from the pure O,O-*trans*-form to a mixture of equal quantities of the two conformers, brings their energies closer together, and lowers the barrier to rotation[97,206]. Introduction of an electron-accepting ester group has the same effect[97,206,207,211,222]. Nevertheless, in contrast to 2-furaldehyde, in the conformationally less mobile 2-aldehydes of thiophen[138,140,141,175,176], selenophen[75,80], and pyrrole[97,148,207] electron-donor substituents have little effect on the position of conformational equilibrium (in these cases almost 100% of the X,O-*cis*-form is present).

5-Substituted 2-acetylfurans, in contrast to the 2-aldehydes, exhibit no clear electronic effects of substituents on the position of conformational equilibrium: electron-donor and electron-acceptor substituents lower the relative content of the X,O-*cis*-form[223].

Substituents at positions 4 and 5 have hardly any effect on the conformations of 2-formyl- and 2-acetyl-thiophens: these derivatives exist in solution[67,92,124,140,176,177] and in the crystalline phase[92,175] in the single planar S,O-*cis*-form. The same situation is found with 4- and 5-substituted formylpyrroles[211].

Infrared spectra and dielectric measurements indicate[196] that 5-substituents have a significant influence on the position of conformational equilibrium in furancarboxylic acids and their chlorides: as in the case of the aldehydes, the content of the O,O-*cis*-form decreases from 100% to 41% on passing from 5-methyl to 5-nitro-derivatives.

Annelation at positions 4 and 5 of the heterocycle should have had the same effect as the introduction of electron-accepting substituents[224]. However, fusion of a benzene ring usually has no significant influence on the conformational equilibrium[54,155]. Conformations similar to those considered above for formyl derivatives of five-membered heterocycles appear also in 2-aldehydes of 4,5-benzo-derivatives of thiophen[225], pyrrole[154,155], and imidazole[73,226].

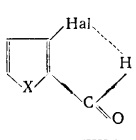
Substitution in the aryl ring of *N*-methylbenzimidazole-2-aldehyde seems unable to change the state of conformational equilibrium[73], whereas ring substitution in pyrrole-2-aldehydes leads in many cases to appearance of a second conformer[159].

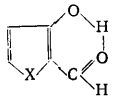
In contrast to *C*-carbonyl derivatives, in the corresponding *N*-derivatives benzannelation has a very substantial effect on the position of conformational equilibrium. Thus whereas in *N*-acetyl- and *N*-formyl-pyrroles the two conformations are equivalent ($\Delta H^{\neq} = 12-13$ kcal mole^{-1}),[212] two planar forms—$H_{(7)}$,O-*cis* and $H_{(7)}$,O-*trans*—can already be distinguished on passing to the corresponding indole and indazole derivatives. In this case the content of one of the conformers may vary within the range 10–90% depending on the nature of the mobile fragment and the substituent. Such

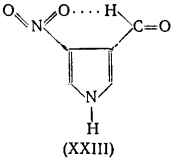
mobility of the position of conformational equilibrium in arene-annelated systems is due to steric effects and is clearly evident in derivatives of *N*-formylbenimidazole and *N*-formylindole[155]. (On further annelation—on passing to symmetrical *N*-carbonyl derivatives of carbazole—the two forms, of course, again become equivalent, as in the case of *N*-formylpyrrole[100].)

Type B

The second type of interaction of the conformationally mobile group (COR) with a substituent comprises direct (electrostatic or dipole–dipole) interaction or other specific effects of a substituent located *ortho* with respect to the COR group. In general steric and electronic effects of substituents may be superimposed on this interaction, but we can isolate quite reliably the specific effects of *ortho*-substituents.


(XXI)


(XXII)


(XXIII)

3-Alkylated and 3-halogenated (XXI) 2-aldehydes of the heterocyclic systems exist predominantly (75–100%) in the X,O-*cis*-form[44,97], but 3-hydroxy-derivatives (XXII) in the X,O-*trans*-conformation[219,227–229]. This is attributed to promotion of the X,O-*cis*-form in (XXI) by a hydrogen bond of type H...Hal, forces of repulsion $O_{carb}...Cl$,[97] and also steric effects of 3-substituents hindering formation of the X,O-*trans*-form. Similarly, a hydrogen bond of type H...O stabilises the *s*-*cis*-form of 4-nitropyrrole-3-aldehyde (XXIII)[97,194,206].

Replacement of the nitro-group by iodine leads to roughly equal contents of the two forms[194]. Such an intermediate position of the conformational equilibrium for 4-iodopyrrole-3-aldehyde is due to I...O repulsive interactions, which destabilise the N,O-*trans*-form, and to the absence of a stable intramolecular hydrogen bond between iodine and aldehydic hydrogen, sufficient to stabilise the *cis*-form[194,206].

The proportion of the O,O-*cis*-form in thiophen-3-aldehyde increases depending on the substituent, and on passing to the 4-bromo(iodo)-derivative reaches 100% owing to Br...H interaction[141,203], but in 4-hydroxythiophen-3-aldehyde falls to zero because of formation of the chelating hydrogen bond $C_{(4)}O–H...O=C$.[203] Similarly, 2-iodothiophen-3-aldehyde exists solely as the S,O-*cis*-form, as a consequence of the characteristics of I...H interaction[141].

It is very significant that introduction of bromine at position 4 in selenophen-3-aldehyde also yields the Se,O-*cis*-form alone, in contrast to the unsubstituted aldehyde, which exists predominantly (80–100%) in the Se,O-*trans*-form[70].

Type C

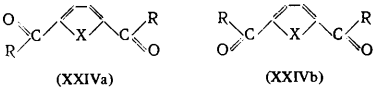
It is a complicated task to isolate in any pure form the steric influence of substituents adjacent to the aldehyde group on the ratio of the conformers, since this group is comparatively small to produce considerable steric hindrance. At the same time the bulky substituents investigated are usually extremely polar, so that their steric influence cannot be segregated from their electronic effects.

Steric effects on the position of conformational equilibrium can be traced more clearly for carbonyl derivatives of *N*-alkylated (*N*-arylated) five-membered heterocycles. The introduction of bulky substituents (e.g.t-butyl) at position 1 in pyrrole-2-aldehyde leads to accumulation of an N,O-*trans*-form or a non-planar conformer in the conformational mixture[152,153,230]. *N*-Aryl (*N*-hetaryl) substituents have a still stronger influence on the conformations of these compounds: *N*-phenyl derivatives of pyrrole[154] exist almost completely in the X,O-*trans*-form, which is not characteristic of the unsubstituted aldehydes.

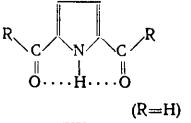
The above examples do not exhaust the whole variety of effects of substituents on conformational equilibrium in carbonyl derivatives of five-membered heteroaromatic systems.

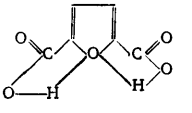
The conformations of dicarbonyl derivatives of five-membered heterocycles must also be discussed in terms of the above three effects. In fact, each carbonyl group, being an electron-accepting substituent, attracts to itself the electron density of the ring and diminishes the conjugation of the other carbonyl group with the heterosystem. Furthermore, adjacent carbonyl groups may promote formation of a particular conformer by electrostatic interaction, specific interactions (e.g. hydrogen bonding), and steric effects.

Introduction of a second carbonyl group into a heterocycle complicates the conformational problem: four conformers or three forms are formally possible in a molecule of symmetry C_2. Of the three conformers

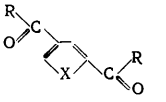

(XXIVa) (XXIVb) (XXIVc)

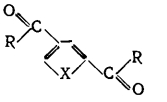
possible for 2,5-diformyl-thiophens[12,108,109,138,140,141,231,232] and -selenophens[70,143] two have been observed: the X,O-*cis*–*cis*-form (XXIVb) predominates or may even be present alone (when X = S)[231,232], and the content of the *s*-*cis*–*trans*-configuration (XXIVa) in the conformational mixture reaches 25%. A similar situation occurs[194,222] in the case of 2,5-diformylpyrrole, but the percentage of the *trans*–*trans*-form (XXIVc) is smaller[222]. It has been suggested[194] that this latter compound exists solely as the N,O-*cis*-form (XXV) stabilised by an intramolecular hydrogen bond.


(R=H)
(XXV)


(XXVI)

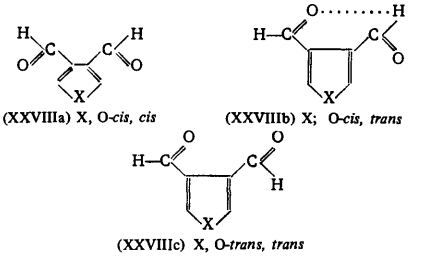
On passing from 2,5-diformyl to the corresponding diacetyl derivatives the proportion of the *s*-*cis*–*trans*-conformers (XXIVa) increases (for the thiophen derivative[140] to 55%). In 2,5-diacetylpyrrole only one carbonyl group forms the N,O-*cis*-structure, while the second is in the *trans*-position[49], which casts doubt on the possibility of a structure of type (XXV) in this case[49,222]. Diesters of 2,5-dicarboxylic acids of these heterocycles contain a mixture of roughly equal quantities of the two conformers[233] (for dimethyl tellurophen-2,5-dicarboxylate the proportion of the *cis*–*trans*-conformer[59] exceeds 50%). Furan-2,5-dicarboxylic acid itself, however, has the O,O-*trans*-structure (XXVI)[42,234].


(XXVIIa) X, O (2)-*cis*, X, O (4)-*cis*


(XXVIIb) X, O (2)-*cis*, X, O (4)-*trans*

In the case of 2,4-dicarbonyl derivatives of the heterocycles only two (XXVIIa,b) of the four possible conformers are present in solution[70,97,138,143]. However, very contradictory values have appeared for their ratio[97,143,235]. Thus selenophen-2,4-dialdehyde has been regarded[143] as existing solely in the *cis*-form (XXVIIa), but has also been assigned[70] the *cis–trans*-configuration (XXVIIb). Similarly inconsistent results have been obtained for the conformations of pyrrole-2,4-dialdehydes: either the $N,O_{(2)}$-*cis*–$N,O_{(4)}$-*cis*-form[143,194] or the $N,O_{(2)}$-*cis*–$N,O_{(4)}$-*trans*-conformer (57%)[97] predominates.

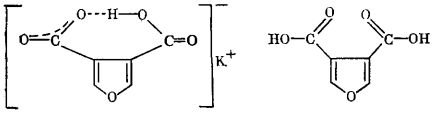
The three planar structures



(XXVIIIa) X, O-*cis*, *cis* (XXVIIIb) X; O-*cis*, *trans*

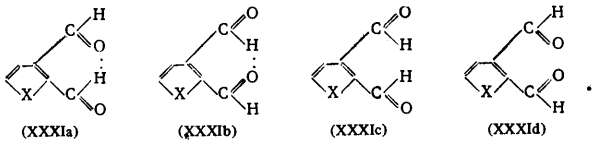
(XXVIIIc) X, O-*trans*, *trans*

are possible in 3,4-diformylhetaryls. The structure (XXVIIIc) is energetically disadvantageous because of the strong Coulombic repulsion of the two carbonyl oxygen atoms. The more advantageous of the remaining two structures is (XXVIIIb), in which additional stabilisation by hydrogen bonding is possible. For this reason the structure (XXVIIIb) apparently predominates in thiophen-3,4-dialdehyde[138], and is the sole form in the selenophen analogue[70,143]. X-Ray results suggest that a similar structure is stabilised by a hydrogen bond also in the anion of potassium furan-3,4-dicarboxylate (XXIX)[117]. In this connection it seems strange that the O,O-*trans*–*trans*-structure (XXX) has been ascribed[236,237] to the acid itself in the crystalline phase.



(XXIX) (XXX)

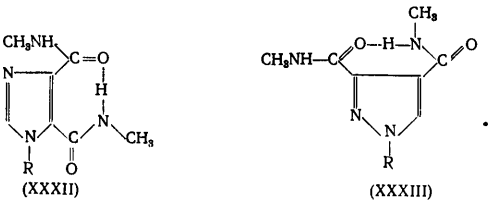
Contradictory results have been obtained also on the conformers of 2,3-dicarbonyl derivatives of five-membered heterocycles. From electrostatic considerations, the most favourable conditions for intramolecular hydrogen bonding, and repulsive interactions, the conformers of 2,3-dicarbonyl derivatives should arrange themselves according to energetic stability in the sequence *cis–cis* (XXXIa) > *trans–trans* (XXXIb) > *cis–trans* (XXXIc) > *trans–cis* (XXXId)



(XXXIa) (XXXIb) (XXXIc) (XXXId)

This conclusion has been confirmed for thiophen-2,3-dialdehyde[70] and ethyl 3-formylpyrrole-2-carboxylate[194]. The view is also held that 2,3-diformyl derivatives of thiophen[138] and selenophen[143] exist predominantly in the *cis–trans*-form (XXXIc). Predominance (70%) of the *trans–cis*-configuration (XXXId) attributed[70] to furan-2,3-dialdehyde therefore appears extremely doubtful.

Results of ^1H n.m.r. infrared spectra, and also theoretical analysis have shown that bismethylamides of the imidazole (XXXII) and pyrazole (XXXIII) series have the structure[22]



(XXXII) (XXXIII)

In the *NN*-dimethylamide of thiazole-2-carboxylic acid only the S,O-*trans*-conformation is populated[200], which is surprising, as neither N,O-*cis*- nor S,O-*trans*-forms are normally characteristic of *o*-carbonyl derivatives. This can be explained both by the steric effect of the dimethylamino-group and by Coulombic attraction between this group and the sulphur atom preventing production of the traditional forms.

4. Influence of Cyclic Heteroatoms

Published information indicates that the nature of the cyclic heteroatom has a significant influence on the position of conformational equilibrium and the stereochemical rigidity of carbonyl-substituted five-membered heterocycles. Coulombic interactions between heteroatom and carbonyl oxygen have a decisive effect on the conformational rigidity of the system, since increase in the positive charge on the former in the sequence X = O, NH, S, Se is accompanied by increase in the $X...O_{CO}$ electrostatic attraction, and hence also stabilisation of the X,O-*cis*-conformer. It must be added that the negative charge on the β-carbon atoms of the heterocycle increases in the same sequence[238], which further stabilises the X,O-*cis*-form by $C_{(3)}...H_{ald}$ Coulombic interaction (in the case of formyl derivatives).

Since in butadiene derivatives the conformer with a *trans*-arrangement of the double bonds relative to the carbon–carbon single bond is thermodynamically the more stable, a similar phenomenon would be expected with carbonyl derivatives of five-membered heterocycles. Indeed, according to the Del Re criterion[243] the weakening of aromaticity in the series of heterocycles containing sulphur, selenium, imino, tellurium, and oxygen, caused by the nature of the heteroatom[71,120,239–242], should tend to increase the role of conjugation, and in the most "dienic" system (furan) lead to the highest content of the O,O-*cis*-conformer for furaldehyde. Experimentally, however, this is not observed: i.e. Coulombic X...O interaction has a greater influence than conjugation in stabilising the conformer.

Quantum-chemical calculations[134] show some increase in energy difference between the two conformers, corresponding to stabilisation of the X,O-*cis*-form, in the series of carbonyl derivatives of furan, pyrrole, thiophen, and selenophen. Attempts to explain[162] stabilisation of certain conformers by dipole–dipole interaction between heterocycle and formyl group have not been confirmed for 2-aldehydes: thus according to theoretical calculation[134] the minimum energy of dipole–dipole interaction corresponds to the energetically less stable X,O-*trans*-conformer. Furthermore, the increases in the positive charge on and the size of the cyclic heteroatom diminish its ability to retain $p_\pi(pd_\pi)$-orbitals and simultaneously enlarge them, so that the contribution of overlap between the heteroatom orbitals and the lone pair of the carbonyl oxygen becomes somewhat greater with selenium than with sulphur; this also favours a more stable partial Se...O bond[244].

The role of the bridging heteroatom X in azole-containing systems has not been investigated separately, but on the basis of published results[73,159,160,218] conclusions can be

transferred from monoheteroatomic to azole rings. On passing from carbonyl derivatives of the fundamental five-membered heterocycles to the corresponding azoles, i.e. on replacing a cyclic methine group by a nitrogen atom, the energy difference between the conformers increases sharply[218]. In the establishment of conformations of *N*- and *C*-carbonyl derivatives of azoles both factors—Coulombic interaction of nitrogen atoms of pyridine type with carbonyl oxygen and minimisation of the energy of the system with the dipoles of the acyl group and of the ring directed antiparallel—play an important part and act together. However, electrostatic $N_{pyr}...O$ repulsion makes a decisive contribution, since on removal of the conformationally mobile group the energy difference diminishes (also the height of the barrier in the case of *N*-acetyl derivatives). In *N*-acetylazoles the "pyrazole" and "imidazole" nitrogen atoms have different roles in the establishment of certain conformers. This example reveals especially clearly the "Coulombic" nature of the stabilisation of rotational isomers. Thus, although the 3-nitrogen atom bears a considerably more negative charge than does the 2-nitrogen atom, the greater distance of the former than of the latter from the carbonyl oxygen leads to appearance of a greater proportion of the $N_{(3)}$,O-*cis*-form in *N*-acetylimidazole than in *N*-acetylpyrazole[104,217].

5. Influence of Nature of Solvent

The influence of the medium, mainly its polarity, on rotational isomerisation and conformational changes is well known. These results have been summarised and supported by numerous examples in an exhaustive review[6]. According to the reactive field model[6] the solvating effect of a solvent can be estimated on the basis of the Onsager theory by means of the formula

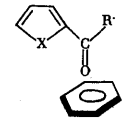
$$\Delta E_i^s = E_i^{vap} - E_i^{soln} = \frac{\mu_i^2}{a_i^3} \cdot \frac{\varepsilon_s - 1}{\varepsilon_s + 2}, \qquad (1)$$

where ΔE_i^S is the energy of solvation for the *i*th conformer of dipole moment μ_i and molecular radius a_i in a medium of dielectric constant ε_S. This equation shows that solvents of high dielectric constant have a greater solvating power and stabilise the more polar conformer. Taking into account the polarisability and the quadrupole moment of the solute molecules yields a more complete expression, regarded[6] as giving the best agreement between theoretical and observed solvation energies. A few other attempts have been made to improve the theory of solvation or to establish a new theory on the same premises[127,245-247].

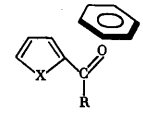
All these investigations involve several postulates restricting their application, but they support the well known rule that a polar isomer is stabilised by a polar solvent. When applied to 2-carbonyl derivatives of five-membered heterocycles, it explains the accumulation of the more polar X,O-*cis*-forms with increase in the dielectric constant of the solvent. Increase in the content of the O,O-*cis*-form with solvent polarity has been shown for 2-furaldehyde[6,202,219,248-251] and its derivatives[85,176,219], as well as for 2-acetylfuran[172] and the chloride and fluoride of furan-2-carboxylic acid[105,196,252].

Special attention should be paid to the work of Abraham[6,251], who has used his theoretical ideas to calculate energy differences between the two conformers of 2-furaldehyde and has compared the results with experimental values. On this basis he has explained the apparently contradictory results for the proportions of conformers in various media. It seems that the *s*-*trans*-form should be stabilised by polar solvents even in the case of carbonyl derivatives of thiophen, selenophen, and tellurophen, but relevant experimental results are lacking. In 2-carbonylpyrroles, on the other hand, the N,O-*trans*-conformer is more polar than the *cis*-isomer. This is why increase in solvent polarity leads in these compounds to stabilisation of the N,O-*trans*-form[97,103,123,147,206,222,253]. However, it must be borne in mind that a general solvation effect cannot explain stabilisation of the N,O-*trans*-form of 5-nitropyrrole-2-aldehyde[194,206] or the peculiar effect of benzene, which stabilises the X,O-*cis*-form of carbonyl derivatives of five-membered heteroaromatic systems more than would be expected from its dielectric constant[6,251] and several other factors[197,219,228].

All these phenomena can be explained by specific solvation effects. Thus the stabilising influence of benzene can be attributed[92] to its electron-accepting properties with respect to carbonyl oxygen. The steric accessibility of the latter is greater in the X,O-*cis*-form (XXXIVa) than in the X,O-*trans*-form (XXXIVb).



(XXXIVa)



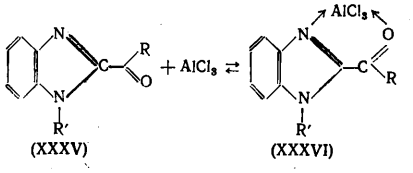
(XXXIVb)

Another example of the specific effect of a solvent on the position of conformational equilibrium is its ability to form intermolecular hydrogen bonds with the solute. Thus dielectric measurements indicate that pyrrole-2-aldehyde contains less of the *s*-*cis*-conformer in dioxan than in benzene solution (73% and 86%). This is attributed[194] to the proton-accepting properties of dioxan, which tend to break the NH...OC type of intramolecular hydrogen bond that usually stabilises the N,O-*cis*-form. Indeed, the content of the *cis*-form of pyrrole-2-aldehyde in dioxan is close to that for *N*-methylpyrrole-2-aldehyde. Similarly, whereas the S,O-*trans*-form of 3-hydroxythiophen-2-aldehyde, stabilised by an intramolecular hydrogen bond, appears in inert solvents[219,228], in proton-accepting solvents the hydrogen bond is broken with formation of the S,O-*cis*-structure.

6. Complex Formation

Interaction with Lewis acids influences significantly the conformations of stereochemically non-rigid systems and in several cases leads to stabilisation of isomers that are uncharacteristic of the free molecules used as ligands. An attempt to relate theoretically the complex-forming power of conformationally mobile ligands with their three-dimensional structure has shown[254] that complex formation is accompanied by a change in conformation only when the sum of the free energies of complex formation and solvation of the complex exceeds in absolute magnitude the sum of the energies of desolvation of the metal ion and the ligand and of spatial reorientation of the latter. This general principle is valid also for carbonyl derivatives of five-membered heterocycles[159,255-258]. Thus the coordination of aluminium chloride yields well defined conformers of 2-formyl derivatives of furan[257] and thiophen[258,259] as well as 2-acetylthiophen[258]. In the case of 2-carbonylazole derivatives complex formation with aluminium chloride may convert the X,O-*cis*-form (XXXV) into

the *trans*-conformation (XXXVI):



(XXXV) (XXXVI)

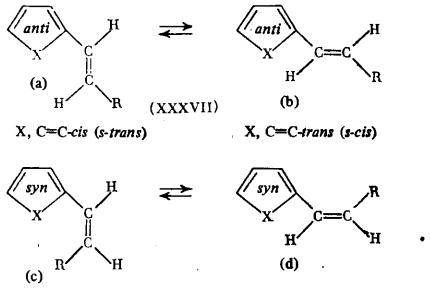
With 2-acetylbenzimidazole (XXXV: R′ = H, R = CH_3), in which the *cis*-form is stabilised by an intramolecular hydrogen bond of type NH...OC, however, this inversion of conformations is not observed. Similarly, conformations characteristic of uncoordinated carbonyl-azoles are preserved[159] even in their complexes with Lewis acids weaker than aluminium chloride—titanium tetrachloride and indium trichloride.

It must be emphasised that many shift reagents are also able to form complexes with carbonyl derivatives of heterocycles. Therefore conclusions concerning the conformations of the above stereochemically non-rigid systems, based on n.m.r. results obtained with the use of shift reagents, must be approached with great caution.

IV. CONFORMATIONAL PROCESSES IN SERIES OF STRUCTURAL ANALOGUES OF CARBONYL DERIVATIVES OF FIVE-MEMBERED HETARYLS

Among structural analogues of the above carbonyl compounds can be included heterocycles containing in the side-chain ethylenic, azomethine, oxime, or thiosemicarbazone groups directly attached to the ring by a single bond. The justification for such inclusion is not only that many of these compounds are obtained from carbonyl derivatives but mainly also that they resemble the latter in possessing multiple bonds capable of conjugation with the heterocycle, so that *s-cis–trans*-isomerism about the single bonds becomes possible.

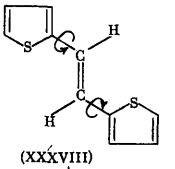
Among representatives of these compounds are hetarylethylenes containing additional substituents attached to the ethylene group and therefore capable not only of *s-cis–trans*-conformational changes but also *syn–anti*-isomerism, e.g.



(XXXVII)

X, C=C-*cis* (*s-trans*) X, C=C-*trans* (*s-cis*)

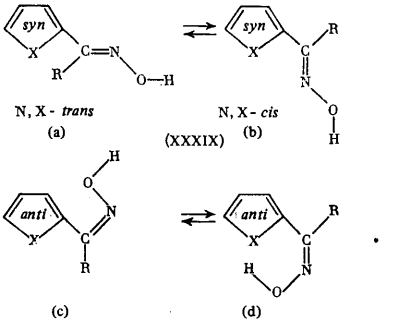
2-Vinyl-furans and -thiophens exist in solution[260–262] solely or predominantly as the *anti*-X,C:C-*cis*-conformer (XXXVIIa), whereas their styryl analogues[235] are present almost completely as the planar X,C:C-*trans*-conformer (XXXVIIb). In the latter the hetaryl and phenyl groups are arranged *anti* with respect to the ethylenic group. If, however, they are located in *syn*-positions, the aryl rings diverge from the ethylene plane because of steric effects. A similar situation is observed with ethylenic derivatives of five-membered heterocycles, i.e. substituted 2-vinyl-furans, -thiophens, and -pyrroles[264–266]. *anti*-1,2-Dithien-2′-ylethylene



(XXXVIII)

exists in the crystalline state as the S,C:C-*cis*-form, with each of the thienyl groups diverging by ~32° from the ethylene plane[267].

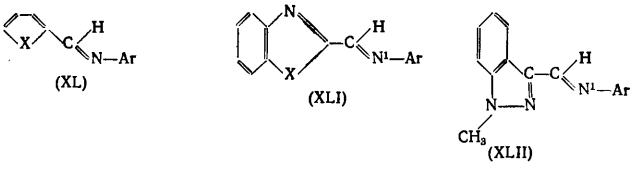
In the crystalline state 5-vinylimidazole exists as a mixture of both planar forms[268]. The thiophen analogues of chalcones exist exclusively in the S,O-*cis*–S,C:C-*cis*-form[269–272], except when a sufficiently bulky substituent is present at position 3 in the heterocycle[270]. Oximes of aldehydes of five-membered heterocycles are also able to exist in two stable isomeric forms—*syn* and *anti* (XXXIXa–d)—for each of which in turn two planar forms—N,X-*cis* and N,X-*trans*—are possible[126]:



N,X-*trans* (a) N,X-*cis* (b) (XXXIX)

(c) (d)

Investigations on oximes of furan (X = O, R = H) by n.m.r. and infrared spectroscopy together with quantum-chemical results have shown[126,273–275] that the N,O-*trans*-conformer is energetically advantageous for the *anti*-form ($\Delta H_{cis-trans}$ = 1.7 kcal mole^{-1} calculated by INDO), and is exclusively present in solution. In contrast, the *syn*-isomer is characterised by the simultaneous presence of two conformers with some predominance of the N,O-*cis*-form (59%), which is energetically more advantageous[276].

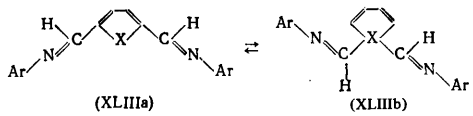


(XL) (XLI) (XLII)

All azomethines containing a five-membered heterocycle as the aldehydic moiety retain the X,N-*cis*-conformation (e.g. (XL)[277] and (XLI)[278,279]) characteristic of the corresponding formyl derivatives¶. Yet an *s-trans–trans*-conformation (XLII) has been very unexpectedly reported[280] for azomethines of 1-methylindazole-3-aldehyde. Equilibrium between the X,N-*cis–cis*-form (XLIIIa) and the X,N-*cis–trans*-form

¶ It must be stressed than anils of six-membered heteroaromatic systems are characterised by the N,N-*trans*-conformation[277].

(XLIIIb) has been found with dianils of thiophen-2,5-dialdehyde:



(XLIIIa) (XLIIIb)

In nitro-derivatives of these compounds the contents of the conformers vary within wide limits (100–40% of the *cis–cis*-form) depending on the position of the nitro-group in the aryl fragment[140]. Removal of the heteroatoms—the cyclic X and oxygen of the N → O group in aldonitrones (VII)



facilitates the appearance of X,O-*trans*-conformers in comparison with the corresponding aldehydes[281,282].

Investigation of the stereochemistry of 2-formylthiophen derivatives[283] suggests that thiosemicarbazones retain the same *cis*-structure as do 2-aldehydes of five-membered heteroaromatic systems.

V. CONCLUSION

Combination of all the above results, despite some inconsistency and in some cases inadequate experimental confirmation, enables several general conclusions to be drawn on the state of the conformational equilibrium in carbonyl derivatives of five-membered heterocycles.

Firstly, there is no doubt of the existence of two planar isomers (*s-cis* and *s-trans*) in the great majority of 2-carbonyl derivatives of furan in solution, with the exception of those cases in which, under the influence of substituents or external conditions, appearance of one of the conformers is energetically disadvantageous or sterically impossible. With few exceptions, but with the same reservations, the corresponding thiophen and selenophen derivatives exist solely in the X,O-*cis*-form. Carbonyl derivatives of tellurophen and pyrrole are conformationally more mobile than those of thiophen, but less mobile than the furan derivatives.

Secondly, several carbonyl derivatives of five-membered heterocycles, in particular ketones, are characterised in most cases by a non-planar structure, with the phenyl group in hetaryl phenyl ketones usually diverging considerably from the trigonal carbonyl plane, while the heterocyclic group is less non-coplanar owing to Het–CO conjugation.

Thirdly, the predominant structure in all carbonyl derivatives of azoles is that in which the carbonyl oxygen atom and the pyridine type of cyclic nitrogen atom are as far apart as possible.

In all cases the predominant structure in carbonyl derivatives of five-membered heteroaromatic systems is governed by Coulombic interaction between the nearest heteroatoms and the carbonyl oxygen atom. Other factors—conjugation between carbonyl and heterocycle, compensation of dipole moments in one of the forms, etc.—can merely be superposed on the dominant Coulombic effect, which is either strengthened or weakened. Despite the many studies of the stereochemistry of carbonyl derivatives of heteroaromatic systems, they exhibit several defects.

1. Compounds have been chosen for investigation without sufficient regard to their relevance. With respect to thoroughness of study (apparently depending on synthetic difficulties) we have, for the same conformationally mobile groups (COR) but different heteroatoms X, the **sequence** O ≈ S ≫ NR > Azoles > Se > Te. The corresponding **sequence** for identical heterocycles but different COR groups is

$$CHO \gg COAlk > COAr > COOH > COHet > COHal > CONH_2 \gg COF.$$

Although the use of carbonyl derivatives of five-membered heterocycles in which X is an element from subgroup VI*b* can be accepted as satisfactory, heteroaromatic systems based on Group V are represented only by nitrogen (pyrrole, azoles).

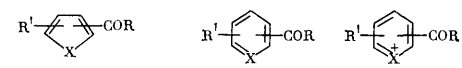
2. Only isolated studies have been made of the influence of external factors (temperature, general and specific solvation, complex formation, state of aggregation) on the position of conformational equilibrium.

3. A weak point is the heterogeneous character of quantitative data on the stereodynamics of *s-cis–trans*-isomeric processes, with inadequate application of quantum-chemical calculations.

4. Too few conclusions on the position of conformational equilibrium have been reached on the basis of the aggregate results of diverse physicochemical and mathematical methods with the use of reliable schemes of theoretical calculation.

All the above defects constitute the main reason for inadequate conclusions concerning the stereochemistry of carbonyl derivatives of five-membered heteroaromatic systems.

In our opinion future research in this field should be concentrated on a more detailed study of the relation between the fine structure of the heterocyclic system and the conformations of carbonyl derivatives. For this purpose the range of compounds studied should include carbonyl derivatives of phosphole, arsenole, and antimonole (XLIV)[284,285].



X = PR^{11}, AsR^{11}, SbR^{11} (XLIV) X = N, P, As (XLV) X = O, S, Se (XLVI)

However, if we approach the more general problem—of studying the stereochemistry of carbonyl derivatives of heteroaromatic systems and their analogues—with use of the information in the present Review and without restriction to results for pyridine derivatives we must investigate the stereodynamics of carbonyl derivatives of six-membered heterocycles (XLV) and (XLVI) and also larger heterocycles[241, 286,287]. The remaining directions of research are clear: the defects formulated under (1)–(4) above must be eliminated (ways for achieving this are quite well known to chemists).

The present survey of *s-cis–trans*-isomerism in five-membered heterocycles shows convincingly that the fine structure of a stereochemically non-rigid system, and also intra- and inter-molecular interactions, are the main factors responsible for the conformations of *s-cis–trans*-isomeric systems. Detailed analysis and generalisation of published information in this field are necessary for the reliable establishment of stereochemically non-rigid structures for various classes of chemical compounds.

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The Chemistry of Antitumour Platinum Complexes

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The antitumour activities of platinum complexes have been characterised in connection with their composition, structure, and properties. A relation has been established between the antiblastoma properties of platinum complexes and the charge and nature of neutral and acido-ligands, the geometrical configuration, and the degree of oxidation of the central atom. Hypotheses are put forward concerning the mechanism of the antitumour activity of platinum complexes. The prospects for the application of platinum and other platinum metal complexes in tumour chemotherapy are assessed.
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I. INTRODUCTION

In many biologically active substances such as haemoglobin, chlorophyll, vitamin B_{12}, and certain enzymes the coordinating atom and active centre is a metal (iron, magnesium, cobalt, copper, zinc, etc.). The need for a comprehensive investigation of the biological activities of complexes, particularly their antitumour properties, is therefore fully justified. The possibility of a wide-scale expansion of such research is supported by the present vast accumulation, in coordination chemistry, of experience on the synthesis of complexes of different metals differing in structure and complexity.

After the publication in 1912 of the communication of Neuberg et al.[1], numerous studies have been carried out in many countries on the search for antitumour substances among metal-containing compounds. In the Soviet Union much work has been done in this field by investigation at the Kiev School of experimental Oncologists, in particular by Magat and coworkers[2], who studied the antitumour properties of the iron tartrate complex. Unfortunately active agents could not be discovered and interest in this branch of the chemotherapy of malignant tumours began to flag. However, in their reviews Larionov and Vermel'[3,4] emphasised that this field should not be forgotten and they believed it useful to investigate metal coordination compounds as potential antitumour agents.

In recent years considerable advances in the search for antitumour preparations were made in the study of organic compounds—alkylating agents, antimetabolities, antibiotics, and plants alkaloids[5,6]. The search for new antitumour prepations has therefore been carried on mainly among these compounds: thus among the 150 000 substances tested at the National Cancer Institute of the USA up to 1970, only 20 were inorganic[7].

The discovery in 1969 by Rosenberg et al.[8] of powerful antitumour properties in *cis*-dichlorodiammineplatinum(II) (henceforth it will be abbreviated to DDP), which is an inorganic substance known since the past century, aroused fresh interest among chemotherapists in metal complexes, particularly platinum complexes. The DDP complex exhibited a pronounced effect on a number of animal and human tumours[9,10].

Since then an intensive search for new antitumour substances has begun in many laboratories of various countries among platinum complexes and studies on the mechanism of their action have been expanded. At the National Cancer Institute of the USA alone approximately 500 different platinum complexes have been investigated towards 1977 [11] and oncological clinical tests have been carried out on five compounds. With each year, the intensity and scale of research into this field of cancer chemotherapy has consistently increased, new laboratories continuously joining in the search. Three International Congresses have been held and more than 1000 communications dealing with various aspects of the antitumour activity of platinum complexes (and certain other metal complexes) under experimental and clinical conditions have been published. Rational ways of synthesising active preparations incorporating coordination compounds are being sought.

On the basis of the authors' own research and literature sources, this review deals with certain problems of the chemistry of platinum complexes with antitumour properties. Particular attention has been devoted to the interrelation between the structure and activity of the compounds, which is one of the most important problems in chemotherapy. The review uses surveys, reports, and symposium and conference proceedings published in recent years[7-10,12-17].

II. CHARACTERISTICS OF THE ANTITUMOUR ACTIVITIES OF PLATINUM COMPLEXES IN RELATION TO THEIR CHEMICAL STRUCTURE AND PROPERTIES

1. Discovery of the Antitumour Activity of Platinum Complexes

The first systematic studies on the antitumour activities of platinum and certain other metal complexes were begun in the USA and the USSR. Using as ligands active antitumour antimetabilities which have already been tested—6-mercaptopurine (Hmp) and butylthiopurine (Butp), Kirschner et al.[18] observed in 1966 the effectiveness of the complexes $Na_2[Pt.(Hmp)_2Cl_4].2H_2O$ and $[Pd(Butp)_3Cl]Cl$ against two strains of mouse tumours. At the same time in 1965–1966 the activity of a number of compounds, particularly platinum and palladium complexes of 6-mercaptopurine and 5-fluorouracil as well as the gold complex of 6-mercaptopurine, was studied at the Institute of Experimental and Clinical Oncology on the Academy of Medical Sciences of the USSR (which has since become the All-Union Oncological Scientific Centre of the

Academy of Medical Sciences of the USSR).[19,20] The palladium and gold complexes of 6-mercaptopurine showed the greatest therapeutic effect:

$[Pd(Hmp)_2]SO_4$—80–92% inhibition of adenocarcinoma AK-755, 50–60% inhibition of Sarcoma 180.
$[Au(Hmp)_3]Cl$—90–95% inhibition of AK-755.

Unfortunately in the above studies[18,20] no advantages were discovered in the activities of the complexes compared with the free antimetabolities and these studies are therefore of merely theoretical interest.

The discovery by Rosenberg of the antiblastoma activity of DDP [8] attracted the attention of investigators to this field and stimulated further search for antitumour agents among metal complexes. By studying the effect of the electric field on a culture of *E.coli*, the authors observed in 1965 the cessation of cell division and the occurrence of unbalanced growth, which was reflected in the lengthening of the microorganisms by a factor up to 300 (the formation of the so-called filamental forms of the bacteria)[21]. The electrolysis was carried out with the aid of platinum electrodes and the nutrient medium contained NH_4Cl, Na_2HPO_4, KH_2PO_4, NaCl, $MgCl_2$, Na_2SO_4, and other ingredients. The study showed that during electrolysis platinum dissolves with formation of a non-electrolytic platinum(IV) complex with a *cis*-structure, which is subsequently reduced in the light to *cis*-$[Pt(NH_3)_2.Cl_2]$ and the latter compound showed a biological activity.

The result of the above investigation[21] was confirmed in a study of the direct effect of *cis*-$[Pt(NH_3)_2Cl_2]$ on tumours[8]. The complex *cis*-$[Pt(NH_3)_2Cl_2]$ (in physiological solution) was administered intra-abdominally on a specific day after transplantation of the tumour; after a time, the mice were killed and the tumour was cut out. The efficiency of the preparation was estimated by comparing the average weight T of the tumours cut out from a batch of mice subjected to chemotherapy and the average weight K of the tumours in mice of a control group; the smaller the ratio T/K, the greater the inhibiting effect of the complex. The following data were obtained in experiments with Sarcoma 180:

Complex	$[Pt(NH_3Cl)_2]$	$[PtEnCl_2]$
Maximum tolerance dose (MTD), mg kg^{-1}	8	16
T/K, %	1	27

Here En is ethylenediamine. The best result was produced by the complex $[Pt(NH_3Cl)_2]$, for which T/K = 1%, which corresponds to 99% inhibition of the growth of the tumour. A considerable proportion of the animals were completely cured. As a result of the primary selection, Rosenberg concluded that non-electrolytic platinum(II) complexes with a *cis*-structure, containing two molecules of a neutral inert ligand (NH_3, amine) and two anions of moderate lability (preferentially Cl^- ions), are biologically active. After a comprehensive experimental investigation of the therapeutic activity and side effects, DDP was subjected to clinical tests and has found extensive applications in the treatment of a number of human tumours, particularly in combination with other antitumour agents[10,22–24].

2. Geometrical Configuration of Non-Electrolytic Platinum(II) Complexes and their Antitumour Activity

Table 1 presents data for the antitumour activities and selectivities of the action of isomeric diacidodiamineplatinum-(II) complexes in relation to two strains of transplantable mouse tumours[7]. The antitumour activity of the complexes administered intra-abdominally single in the maximum tolerance dose (MTD), on Sarcoma 180, was determined 10 days after the injection and was expressed as a percentage inhibition of the growth of the neoplasm. The selectivity of the action of the substances was investigated on mice with plasmacytoma ADJ/PC6 using the same schematic arrangement of the experiments and was expressed by the therapeutic index $TI = LD_{50}/ED_{90}$, where ED_{90} is the effective dose resulting in 90% inhibition of the growth of tumours on the tenth day after injection. The higher the TI, the greater the antitumour activity and the smaller the toxic effect of the substance on the organism.

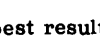
The data presented in Table 1 in relation to isomeric complexes with different amines and acido-ligands fully confirmed the conclusion that, when the complex exhibits antiblastoma activity, the latter is characteristic only of the *cis*-isomer; the *trans*-isomers have no antitumour properties (TI = 1).

Since this conclusion is general, the search for new antitumour platinum preparations attention was concentrated on the synthesis of non-electrolytic compounds with the *cis*-structure (Table 2). Such complexes are obtained particularly readily when potassium or sodium chloroplatinites are treated with bidentate amines which combine with platinum like ethylenediamine. Among them, complexes with 1,2-diaminocyclohexane proved to be the most promising.

Table 1. The influence of the geometrical isomerism of non-electrolytic platinum(II) complexes on their antitumour activities[7,17].

Complex	Medium	Dose range, mg kg^{-1}	Toxic limit, mg kg^{-1}	T/K, %	Dose, mg kg^{-1}
cis-$[Pt(NH_3Cl)_2]$	*S*	0.5—20	8	1	8
trans-$[Pt(NH_3)_2Cl_2]$	*S*	2.5—40	40	85	2.5—40
cis-$[Pt(CH_3NH_2Cl)_2]$	*S*	10—30	12—20	25	15
trans-$[Pt(CH_3NH_2)_2Cl_2]$	*S*	5—100	25	100	5—20
cis-$[Pt(C_2H_5NH_2Cl)_2]$	*S*	5—50	45	14	40
trans-$[Pt(C_2H_5NH_2)_2Cl_2]$	*S*	5—20	20	105	5—20
cis-$[Pt(NH_3Br)_2]$	*B*	5—20	15	30	14
trans-$[Pt(NH_3)_2Br_2]$	*B*	10—40	40	110	10—40

ADJ/PC_6 plasmacytoma

Complex	Medium	Dose range, mg kg^{-1}	LD_{50}, mg kg^{-1}	ED_{90}, mg kg^{-1}	TI
cis-$[Pt(NH_3Cl)_2]$	*A*	0.1—40	13.0	1.6	8.1
trans-$[Pt(NH_3)_2Cl_2]$	*A*	0.1—40	27.0	>27.0	<1.0
cis-[Pt( $NHCl)_2$]	*A*	2.5—160	56.5	2.6	21.7
trans-[Pt( $NH)_2Cl_2$]	*A*	2.5—160	18.0	>18.0	<1.0
cis-[Pt( $NHCl)_2$]	*A*	3—200	140	10.8	13.1
trans-[Pt( $NH)_2Cl_2$]	*A*	3—200	72	>72	<1.0

Notation: *S* = 0.13 M NaCl; *B* = 0.04 M NaBr; *A* = suspension in groundnut oil.

It is seen from the data in Table 2 that, despite their *cis*-configuration†, some of the complexes show little activity in relation to the plasmacytoma (TI ≅ 2).

† We shall either indicate the geometrical configuration of the isomers (*cis*- or *trans*-) or shall employ the coordination formulae, for example *cis*-$[Pt(NH_3Cl)_2]$ and *trans*-$[Pt(NH_3)_2.Cl_2]$.

3. The Nature of the Acido-Ligand in the *cis*-Isomers

Among the complex *cis*-non-electrolytes with monodentate acido-ligands, the chloride ligands exhibit a high activity. Thus, in relation to sarcoma 180, the activity varies in the following sequences[7]:

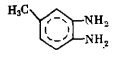
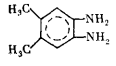
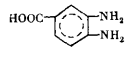
$$[Pt(NH_3X)_2]$$

X:	$Cl^- > Br^- > SCN^- > NO_2^- > I^-$				
T/K:	1	30	70	99	110

$$[PtEnX_2]$$

X:	$Cl^- > Br^- > NO_2^- > I^- \cong SCN^-$				
T/K:	4	31	71	82	83

Table 2. The activities of certain new complexes of the type $[PtLCl_2]$ with bidentate ligands against plasmacytoma ADJ/PC6.[25–27]

Ligand L	LD_{50}, mg kg^{-1}	ED_{90}, mg kg^{-1}	TI
	14.1	2.1	6.9
	48	2.4	20
	22.5	3.7	5.3
	283	2,5	113
	180	90	2

The Pt–X bond strength increases from Cl^- to I^-, which can be seen from the decrease of the overall instability constant and the decrease of the positive standard free energy:

	$[PtCl_4]^{2-}$	$[PtBr_4]^{2-}$	$[PtI_4]^{2-}$	References
K_{inst}	$2.5 \cdot 10^{-17}$	$4 \cdot 10^{-21}$	$2.5 \cdot 10^{-30}$	[28,29]
ΔG°, kcal mol^{-1}	+ 34.40	+ 31.80	+ 18.40	[30]

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

These data indicate the opposite variation of the Pt–X bond strength and the activity of the complex. Complexes with carboxylate ions bound as bidentate species, of the type $[Pt(NH_3)_2X$ and $[PtEnX]$, exhibit an appreciable activity, malonate and substituted malonate complexes (T/K = 7–12%) being more active than the oxalate complexes (T/K = 25–26%).[7] It was found unexpectedly that, in contrast to $[Pt(NH_3)_2 \cdot (C_2O_4)]$, the complex $[PtEn(C_2O_4)]$ exhibits a curare-like activity, like the aquo-cationic complexes. Under the usual conditions, $[PtEn(C_2O_4)]$ is not hydrolysed; the complex apparently undergoes enzymatic hydrolysis in the organism. The compounds $[Pt(NH_3)_2(N_2O_2)]$ and $[PtEn(N_2O_2)]$ were the first complexes with a cyclic acido-ligand, namely the hyponitrite ion $N_2O_2^{2-}$, to be isolated[31].

The antitumour activities of these compounds were studied in relation to three strains of transplantable mouse tumours: adenocarcinoma 755, the Lewis lung cancer (LLC), and leukaemia L-1210. The complexes were dissolved in a physiological solution and were administered to mice intra-abdominally in the maximum tolerance doses. The activity of both hyponitrite complexes was tested on adenocarcinoma 755 (73–80% inhibition of the growth of tumour in relation to the control). In constrast to $[PtEn(C_2O_4)]$, the complex $[PtEn \cdot (N_2O_2)]$ does not exhibit neurotoxicity[32].

The influence of the nature of the acido-ligand on the antitumour activities on a series of non-electrolytic *cis*-complexes of platinum(II) with 1,2-diaminocyclohexane have been studied in detail[33,34] in relation to 15 acido-ligands (Table 3). The activity M was estimated from the formula

$$M = \frac{LD_{50} \times ILT_{opt}}{ID_{99.9} \times 100},$$

where $ID_{99.9}$ is the dose killing 99.9% of the tumour cells and ILT_{opt} is the optimum increase of lifetime (expressed as a percentage). The greater the value of M, the higher the activity of the complex.

Table 3. The activities of non-electrolytic *cis*-complexes of platinum(II) with 1,2-diaminocyclohexane and various acido-ligands against lympholeukaemia L-1210.[33,34]

Ligand	SO_4^{2-}	OH^-	$B_4O_7^{2-}$	$C_2H_5SO_4^-$	$NH_2SO_3^-$	NO_3^-	Cl^-
M, %	100	80	70	50	30	22	18
Ligand	HPO_4^{2-}	SO_3^{2-}	BrO_3^-	SeO_4^{2-}	SiF_6^{2-}	NO_2^-	CNO^-
M, %	14	14	32	7	3	1	0

The sulphide complex is the most active (M = 100%). In this case complexes with less strongly bound acido-ligands also proved to be more active; the activity decreases in the sequence $SO_4^{2-} > B_4O_7^{2-} > C_2H_5SO_4^- > NO_3^- > Cl^-$. The change in the nature of the acido-ligand is reflected not only in the bond strength but also in the solubility of the complex, which influences in its turn its antitumour properties. The complexes of this series are in most cases more soluble and more active.

4. The Nature of the Amine in the *cis*-Isomers

The replacement of NH_3 by amines of different structure greatly alters the activity of the complex; an idea about this can be obtained from Table 1. Thus, in relation to sarcoma 180, the aliphatic amines CH_3NH_2 and $C_2H_5NH_2$ lower the activity of the complex. Aniline and pyridine have little effect on the activity.

The plasmacytoma ADJ/PC6 proved to be extremely sensitive to the nature of the amine in *cis*-$[Pt(ACl)_2]$. Table 4 presents data for the activities of complexes of this type containing NH_3, methyleneamine, heterocyclic bases (aziridine and pyrrolidine), and a number of alicyclic amines (the complexes with amines are sparingly soluble in water and were administered to mice intra-abdominally in the form of a suspension in grount-nut oil). The replacement of NH_3 by heterocyclic bases improved the result by a factor of 2–3. The activity increases particularly markedly following the introduction of alicyclic amines: TI increases up to 200 (cyclopentylamine) or 267 (cyclohexylamine). The increase

of TI is caused by the sharp reduction of the toxicity of the complexes: LD_{50} is 3200 mg kg^{-1} for cyclohexylamine and 13 mg kg^{-1} for NH_3, but the inhibiting activity (ED_{90}) changes only slightly.

Table 4. The influence of the nature of the amine on the antitumour activities of non-electrolytic *cis*-complexes of platinum(II) against plasmacytoma ADJ/PC6.[7,26]

Amine	LD_{50}, mg kg^{-1}	ED_{90}, mg kg^{-1}	TI
The complexes $[Pt(ACl)_2]$			
NH_3	13.0	1.6	8.1
CH_3NH_2	18.5	18.5	1.0
	56.5	2.6	21.7
	140	10.8	13.1
	56.5	2.8	24.6
	67	6	11
	480	2.4	200
	3200	12	267
	625	1.8	35
	660	230	2.9
The complexes $[PtACl_2]$			
	14.1	2.1	6.9
	48.0	2.4	20.4
	283	2.5	113

Such high therapeutic indices are not enountered among other antitumour preparations. The result is hopeful, since, by altering the composition of the complex, it is possible to obtain fairly effective and relatively non-toxic preparations. The disadvantages of the complexes with alicyclic ligands are their low solubility, which hinders their clinical use and a narrower therapeutic spectrum than for DDP; thus their activity in relation to Sarcoma 180 and L-1210 is low. The complex with cyclopentylamine exhibits the most comprehensive activity. The complexes with alicyclic diamines (1,2-diaminocyclohexane) are also active in relation to L-1210. At the same time, one should note that in many instances it is difficult to reach unambiguous conclusions concerning the influence of the nature of the amine or the substituent on the activity of the complex, the effect depends on the tumour strain. For example, $[Pt(PyCl)_2]$ [35] is active towards Ehrlich ascites carcinoma but its activity towards Sarcoma 180 is low. The activity of the complex is also sensitive to the structure of the ligand: the complex $[PtLCl_2]$ containing *trans*-1,2-diaminocyclohexane is more active than the complex with *cis*-1,2-diaminocyclohexane, the activity being a maximum for the complex with the laevorotatory *l-trans*-isomer[36].

In coordination chemistry the reactivity of complexes is usually attributed to the electronic structure of the ligands—their σ-donor and π-acceptor properties. It is difficult to make a comparison of this kind for the antitumour activity, since the latter is determimed not only by chemical and physicochemical characteristics but also by other factors—the lyophilic and lyophobic properties of the complexes, the permeability of cell membranes to them, and pharmacokinetic parameters.

5. The Solubility of the *cis*-Non-Electrolytes

The majority of dichlorodiamineplatinum(II) complexes are sparingly soluble in water and yet a fairly high solubility of complexes is necessary for intravenous injections. The efforts of investigators have therefore been directed to the synthesis of soluble active complexes (Table 5).

Table 5. The influence of the acido-ligand and substituents on the solubilities of the complexes in water at room temperature (L = 1,2-diaminocyclohexane).[7,26,30]

Complex	Solubility, g/100 ml H_2O	Complex	Solubility, g/100 ml H_2O
$[PtEnCl_2]$	0.08	$[Pt(NH_3Cl)_2]$	0.22
[PtEnmal]	1.00	$[Pt(NH_3)_2mal]$	0.04
$[PtEn(C_2H_5\text{-mal})]$	0.10	$[Pt(NH_3)_2(CH_3\text{-mal})]$	0.25
$[PtLCl_2]$	0.10	$[Pt(NH_3)_2(C_2H_5\text{-mal})]$	0.59
[PtLmal]	0.5	$[Pt(\text{iso-}PrNH_2)_2Cl_2]$	0.10
[PtL(OH-mal)]	1.5	$[Pt(\text{iso-}PrNH_2)_2mal]$	3.50

Table 6. Comparison of the solubilities of complexes of the types $[PtL'X_2]$ and $[PtL''X_2]$ (L' = 1,2-diaminocyclohexane and L'' = *o*-phenylenediamine) and their antitumour activities (against L-1210).[37,38]

X in complex $[PtL'X_2]$	Solubility at 25 °C, mg ml^{-1}	M, %	X in complex $[PtL''X_2]$	Solubility at 25 °C, mg ml^{-1}	ILT, %
$BrCH_2COO^-$	1	200	$1/2\ SO_4^{2-}$	5	100
$1/2\ SO_4^{2-}$	3	100	NO_3^-	5	48
$1/2\ mal^{2-}$	0.5	23	$BrCH_2COO^-$	5	43
Cl^-	0.1	18	$1/2\ mal^{2-}$	0,25	23

An increase of the solubility in water can be achieved in the following way: (1) by replacing Cl^- ions by cyclic carboxylate ions, for example malonate and its derivatives; (2) by introducing hydrophilic groups into the ligand; (3) by employing less strongly bound acido-ligands; (4) by using platinum(IV) complexes (but not in all cases). The replacement of $2Cl^-$ by mal^{2-} in the complexes where L = 1,2-diaminocyclohexane or other diamines increases the solubility by a factor of 5–10 (Table 6). This has also been observed to a lesser extent for ammines (with the exception of the replacement of $2Cl^-$ by mal^{2-}). The reason is apparently that in the case of a cyclic acido-ligand the intermolecular bonds are weakened and the lattice energy is lower.

The introduction of an organic substituent (C_2H_5) lowers the solubility of the complex and the introduction of the lyophilic OH group increases it. The increase of the hydrolysability of the complex in the case of less strongly bound ligands (SO_4^{2-} and NO_3^-) also promotes an increase of the solubility of the complexes with 1,2-diaminocyclohexane [33,34,37,38] (Table 6).

The activities of the complexes $[PtL'X_2]$ increases in the following sequence of L': $\frac{1}{2}SO_4^{2-} > OH^- > \frac{1}{2}B_4O_7^{2-}$; their solubilities in water at 40 °C decrease in the same sequence[33]. Hence one can conclude that the more soluble complexes are more active. However, this is not always so; in a series of complexes with branched aliphatic amines and alicyclic amines the less soluble complex is less toxic and therefore has a higher therapeutic index TI.[27]

The antitumour activities have been compared with non-aqueous, lipid solubilities, since the latter are related to the permeability of the membranes to the complexes. For this purpose, the solubilities of the complexes are determined in 1-octanol or chloroform by extremely sensitive methods—the atomic absorption and fluorescence methods[27]. In the series with alicyclic amines complexes with cyclopentyl- and cyclohexyl-amines, whose solubilities in water and chloroform are comparable—the partition coefficients K_{CHCl_3/H_2O} are 0.88 and 0.84—have the best TI. Unfortunately there are many discrepancies, particularly for DDP, where TI = 8 and $K_{CHCl_3/H_2O} = 0.008$. Therefore it is at present difficult to make any predictions about the activity of the complexes on the basis of their partition coefficients between non-aqueous and aqueous phases. One thing is certain, namely that intravenous injections in clinical tests require complexes which are fairly soluble in water.

6. The Nature of the Donor Atom in the Neutral Ligand

The relacement of amines by phosphorus- or sulphur-containing ligands [$P(C_6H_5)_3$, DMSO, $S(C_2H_5)_2$, etc.] in the *cis*-isomers $[Pt(ACl)_2]$ leads to the disappearance of activity: the percentage inhibition of the growth of Sarcoma 180 is in the range 40–20.[7] These ligands exhibit a powerful *trans*-influence. It may be that this entails a marked increase of the mobility of the Cl^- ion in the *trans*-position with respect to the ligand and an increase of the capacity of the complex for non-specific reactions, as in the case of *trans*-$[Pt(NH_3)_2.Cl_2]$. The complex with the cyclically bound glycimate ion, i.e. $[Pt(NH_2CH_2COO)_2]$, is also inactive.

7. The Antitumour Activities of Charged Platinum(II) Complexes

It was mentioned above that antitumour activity is characteristic of non-electrolytic platinum(II) complexes which permeate most effectively through the cell membrane. In 1975 Davidson, Rosenberg, and coworkers[39] observed an antitumour activity in complexes differing in structure from the non-electrolytic complexes—the so-called "platinum pyrimidine blues". These substances are obtained by keeping a solution of $[Pt(NH_3H_2O)_2](NO_3)_2$ at 37 °C in contact with 2,4-dihydroxypyrimidines—uracil, thymine, and their derivatives (Table 7). Amorphous blue or green precipitates are isolated from the resulting blue solution by adding alcohol and cooling. The chemistry of "pyrimidine blues" has not been investigated; only their overall composition is known. The majority of the analyses correspond to the ratios Pt : NH_3 : pyrimidine : OH = 1 : 2 : 1 : 1. It has been observed by electrophoretic and chromatographic methods that platinum pyrimidine blues contain platinum in the form of a cation and have the structure $[Pt(NH_3)_2(pyrimidine)]X_n$, where X = NH_3^-, CH_3COO^-, $\frac{1}{2}SO_4^{2-}$, Cl^-, etc.[40] They form blue precipitates with a number of anions [for example, $B(C_6H_5)_4^-$, PF_6^-, or $P_2O_7^{4-}$]. Thus these compounds belong to the class of the few active cationic complexes.

The "blues" are mixtures of polymeric species whose molecular weight is in the range 1000–3000. Bridging hydroxo- and olate groups and base anions are involved in the polymerisation.

According to X-ray electron spectroscopic data, the "blues" contain platinum(II) (ionisation energy $E_{Pt\ 4f}$ = 74 eV). At the same time the paramagnetic properties of these compounds are attributed to the presence of platinum-(III), the content of which can reach 25%, which corresponds to an average degree of oxidation of platinum of 2.25.[40,41] Approximately 70 complexes of the "blues" type have been studied in relation to several strains of mouse tumours. Among them 14 complexes showed a higher therapeutic effect against Sarcoma 180 than DDP (see Table 7).

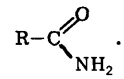
Table 7. The antitumour activities of platinum pyridimine "blues" (against ascites Sarcoma 180).[39,42]

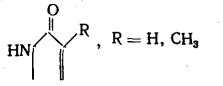
Complex	Toxic dose, mg k^{-1}	ILT, %	Single dose, mg kg^{-1}	Number of cured mice/number of experimental mice
cis-$[Pt(NH_3Cl)_2]$	10	49	7	1/12
Platinum pyridine "blues"				
Uracil	400	91	200	5/6
5,6-Dihydrouracil	400	92	200	4/6
6-Methyluracil	800	87	600	3/6
5,6-Dimethyluracil	400	100	400	5/6
5-Fluorouracil	100	90	100	4/6
Free 5-flurouracil		8	60	0
5-Chlorouracil	200	67	50	3/6
Thymine	450	72	300	2/6

The advantages of the "blues" include high solubility in water (5% against 0.1% for DDP) and a lower toxicity than that of DDP (LD_{50} = 200–500 mg kg^{-1}, the corresponding value for DDP being 12–14 mg kg^{-1}). The activity of the platinum(II) complex of 5-fluorouracil is much higher than that of the free ligand[39]. Biochemical and electron-microscope studies have shown that the "blues" hardly interact with proteins but are strongly bound by nuclear DNA; with their aid, it is possible to "label" DNA and to follow the changes in it[40,41].

It has been suggested[39] that the mechanism of the action of the "blues", which are charged complexes, differs from that of the non-electrolytes.

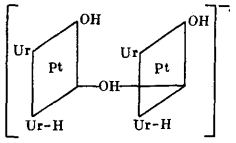
"Blues" of another type, formed when aliphatic nitriles RCN are treated with silver nitrate and kept at 37 °C for 4–6 days, have also been isolated. Blue substances insoluble in acetone exhibited the most effective antitumour properties—they increased the lifetime of mice with ascites Sarcoma 180 by 90%. It has been suggested that the nitrile is slowly hydrolysed, which yields platinum complexes of amides


. Uracil and thymine, which give rise to "pyrimidine blues", also contain a fragment having a similar structure[43]:



Also one monomeric cationic complex, which does not belong to the class of the "blues", has been found to be active[44]. The complex with spermine, a tetradentate polyamine, is active against leukaemia R-388, but is inferior to *cis*-dichlorodiammineplatinum as regards the inhibiting effect.

Certain anionic platinum(II) complexes have also been found to be active[45]. The interaction of the non-electrolytic urea complex *trans*-$[PtUr_2Cl_2]$ in an alkaline medium (pH ~ 9.5) is accompanied by the formation of an intensely blue solution, from which blue precipitates, having the composition $M[Pt_2Ur_2(Ur-H)_2(OH)_3]$, where $M = Na^+$ or K^+ and (Ur − H) is a deprotonated urea molecule, are isolated by the addition of alcohol. These substances are readily soluble in water; the complex anion remains unchanged in double decomposition reactions, which follows from the isolation of blue sparingly soluble precipitates with silver(I) and thallium(I) salts. The ionisation energy of platinum $E_{Pt\ 4f} = 73.3$ eV (according to data obtained by Nefedov[45] at the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences), which corresponds to the +2 oxidation state of platinum. The electron absorption spectrum of an aqueous solution of the complex is characterised by an absorption band with $\lambda_{max} = 620$ nm and $\varepsilon_{max} = 3300$. The complexes are stable in aqueous solutions; the absorption spectrum does not change for 24 h. The position of the absorption band of these "anionic blues" differs from that of the cationic pyrimidine blues ($\lambda_{max} = 752$ nm) [40] and is close to that observed in the spectra of the blue complexes obtained on treatment of potassium chloroplatinite with the monoamide of oxalic acid $NH_2COCOOH$ ($\lambda_{max} = 620$–625 nm).[46] The following structure with two terminal and one bridging OH groups can be proposed for the anionic complexes[45]:



The anionic comples $K[Pt_2Ur_2(Ur-H)_2(OH)_3]$ has been tested for antitumour activity in relation to six strains of transplantable mouse tumours: lympholeukaemia L-1210, haemocytoblastoma La, plasmacytoma MOPC-406, the mammary gland adenocarcinoma (AK-755), the large intestine adenocarcinoma (AKATOL strain), and the flat cell cancer RshM-5 of the neck of the uterus[45]. It has been established that the complex is relatively non-toxic: the single maximum tolerance dose is in excess of 500 mg kg^{-1}. An appreciable antitumour activity of the anionic complex has been noted in relation to three strains of solid mouse tumours: AK-755 (85% inhibition of the growth of tumour), RShM-5 (81%), and AKATOL (55%). The complex proved to be inactive in relation to the two leukaemias and the plasmacytoma MOPC-406.

The above examples show that the "charge prohibition" is not insurmountable: there exist cationic and anionic complexes with a definite activity, although smaller than that of the non-electrolytic complexes. It is of interest that the active cationic and anionic complexes have a polymeric structure.

8. The Antitumour Activity of Platinum(IV) Complexes

Two active non-electrolytic platinum (IV) complexes have been described[8,9]: *cis*-$[Pt(NH_3)_2Cl_4]$ and $[PtEnCl_4]$. It has been suggested that these compounds are reduced in a biological medium to platinum(II) complexes which constitute the active principle. The possibility of such reduction follows from a comparison of the oxidation-reduction potentials of these compounds in a biological medium for which $E^0 = 0$ to 0.5 V:[30,47]

	E°, V
$[PtCl_6]^{2-} + 2e \rightleftarrows [PtCl_4]^{2-} + 2Cl^-$	+0.77
$[PtBr_6]^{2-} + 2e \rightleftarrows [PtBr_4]^{2-} + 2Br^-$	+0.64
cis-$[Pt(NH_3)_2Cl_4] + 2e \rightleftarrows$ *cis*-$[Pt(NH_3)_2Cl_2] + 2Cl^-$	+0.67
$[PtEnCl_4] + 2e \rightleftarrows [PtEnCl_2] + 2Cl^-$	+0.684

Analogous processes take place also with rhodium(III) complexes in a biological medium, where they are reduced to active rhodium(II) complexes[48].

The platinum(IV) complexes are more stable and more inert than the platinum(II) complexes, so that the attention of investigators has been concentrated on the latter. However, it has been suggested that the platinum(IV) complexes permeate more readily through a membrane. The interest in the platinum(IV) complexes increased after it had been discovered that certain non-electrolytic platinum(IV) complexes, namely the tetrachloro-complexes $[PtA_2Cl_4]$ and particularly the dihydroxo-complexes $[PtA_2Cl_2(OH)_2]$ dissolve more readily than the initial dichlorodiammineplatinum(II) complexes. In certain cases oxidation results also in an increase of solubility in $CHCl_3$, which characterises the behaviour in relation to lipids[27].

Unfortunately, comparison of the inhibiting activities and toxic properties of the platinum(II) and platinum(IV) complexes does not allow an unambiguous conclusion concerning the change in these characteristics on oxidation. Thus the platinum(IV) complexes with alicyclic ligands[27] and with 1,2-diaminocyclohexane[38] are less active and more toxic than the platinum(II) complexes. At the same time the toxicity of the platinum(IV) complexes with L = NH_3 or iso-$C_3H_7NH_2$ is smaller; for L = NH_3, the therapeutic activity of the platinum(IV) complexes is also greater.

Table 8. The antitumour activity of the complex $[Pt(NH_3Cl)_2.(OH)_2]$.

Dose, mg kg^{-1}	Interval, h	Number of injections	Increase of life of mice, %%		Inhibition of the growth of tumours on 10th day after therapy, %%		
			L-1210	haepatoma 22 (ascites)	AK-755	AKATOL	Sarcoma 180
50		1	50	*	96	45	76
25	24	5	90	*	83	87	76
15	24	5	90	160	83	87	*

*Not investigated.

In 1977 two groups of investigators discovered simultaneously and independently (in the USSR [49] and in England[27]) the high activity of the complex $[Pt(NH_3Cl)_2(OH)_2]$, which is not inferior to that of DDP. Konovalova et al.[49] investigated the compound in relation to five strains of transplantable mouse tumours and leukaemias (Table 8), while Tobe and Khokhar[27] tested it only on the plasmacytoma ADJ/PC6.

It is noteworthy that the complex $[Pt(NH_3Cl)_2(OH)_2]$ is ten times less toxic than DDP. This compound is now being investigated in depth at the All-Union Oncological Scientific Centre of the Academy of Medical Sciences of the USSR; it has been shown that the *trans*-isomer of this compound is inactive[49].

It is of interest that the anionic platinum(IV) complexes of the type $(NH_4)_2[PtHal_4(OH)_2]$ exhibit[50b] a definite activity; the maximum activity was found in $(NH_4)_2[PtBr_4(OH)_2]$. This compound appreciably inhibited (by 70%) the growth of the mouse mammary gland adenocarcinoma (strain AK-755) and increased by 65% the life of animals with leukaemia L-1210. The authors[50] explained this by the fact that the bromide-containing platinum(II) anions are more readily reduced than the chloride-containing anions and are more labile than the iodide-containing anions.

Thus the majority of investigators are inclined to the view that the mechanism of the action of the non-electrolytic platinum(IV) complexes includes a stage of their preliminary reduction to the platinum(II) complexes. However, one cannot rule out completely also the possibility of the direct action of the platinum(IV) complexes on tumour cells: two platinum(IV) complexes with substituted ethylenediamines, namely $[PtACl_4]$, are active [it has been found that TI = 3.05 for A = $(CH_3)_2N(CH_2)_2NHCH_3$ and TI = 1.7 for A = $(CH_3)_2.N(CH_2)_2N(CH_3)(C_2H_5)$], while the corresponding and non-electrolytic platinum(II) complexes are inactive[30].

9. The Most Promising Complexes

Summarising the available literature data, it is possible to distinguish approximately 30 most active non-electrolytic platinum(II) and platinum(IV) complexes with ammonia, amines, and various acido-ligands.

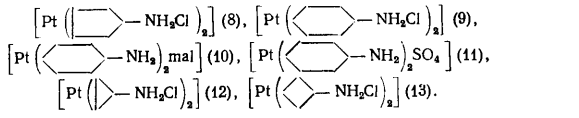
I. Platinum(II) complexes with NH_3:

$[Pt(NH_3Cl)_2]$ (1), $[Pt(NH_3)_2C_2O_4]$ (2), $[Pt(NH_3)_2mal]$ (3), $[Pt(NH_3)_2N_2O_2]$ (4), $[Pt(NH_3)_2L]$ (L = cyclobutane-1,1-dicarboxylate anion) (5).

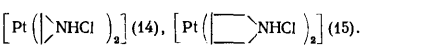
II. Platinum(II) complexes with aliphatic monoamines:

$[Pt(iso\text{-}C_3H_7NH_2Cl)_2]$ (6), $[Pt(iso\text{-}C_5H_{11}NH_2Cl)_2]$ (7).

III. Platinum (II) complexes with alicyclic monoamines:



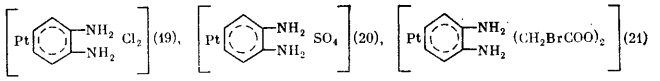
IV. Platinum(II) complexes with heterocyclic monoamines:



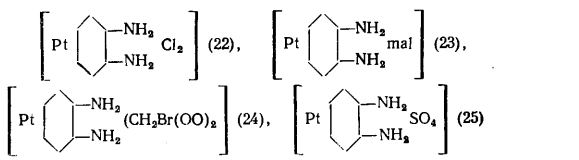
V. Platinum(II) complexes with aliphatic diamines:

$[PtEnCl_2]$ (16), $[PtEn\,mal]$ (17), $[PtEnN_2O_2]$ (18).

VI. Platinum(II) complexes with aromatic diamines:



VII. Platinum(II) complexes with alicyclic diamines:



VIII. Platinum(IV) complexes:

$[Pt(NH_3)_2Cl_4]$ (26), $[PtEnCl_4]$ (27), $[Pt(NH_3Cl)_2(OH)_2]$ (28), $[Pt(iso\text{-}C_3H_7NH_2Cl)_2(OH)_2]$ (29).

IX. Platinum pyrimidine blues and certain other charged complexes (30).

However, as regards clinical tests, only approximately half of these compounds are promising: the complex must exhibit a high activity against a wide spectrum of experimental tumours, should be relatively non-toxic, and should be fairly soluble in water. Complexes (1), (5)–(13), (22)–(26), (28), and (29) possess a set of such properties to a smaller or greater extent; some of these compounds are now passing through various stages of clinical tests. The effect of DDP has been studied in detail and the second phase of tests is being completed; more than 1000 patients have been treated with this compound. Detailed data concerning the results of the clinical tests on the complexes as well as their toxic properties and the measures taken to eliminate them have been published in a review[10].

III. THE MECHANISM OF THE ANTITUMOUR ACTIVITY OF PLATINUM COMPLEXES

One of the main requirements which must be met by the experimental and clinical chemotherapy of malignant tumours is selectivity of action of the therapeutic agents on the cells of the cancer tumour and the smallest possible damaging effect of such agents on the normal cells. Compared with normal cells, tumour cells are characterised by a higher level of synthesis of DNA and the action of a number of antitumour preparations, particularly alkylating agents, is in fact directed to such macromolecules.

Molecular-biological studies *in vitro* using tritium-labelled thymidine, uridine, and leucine[51,52] and experiments *in vivo*[53] have shown that the complex $[Pt(NH_3Cl)_2]$, which exhibits an antitumour activity, selectively suppresses the synthesis of DNA but has little effect on the synthesis of RNA and proteins. Thus the target attacked by the platinum complexes in the organism has been identified at the intermolecular level.

There exist several points of view concerning the causes of the different antitumour activities of platinum complexes of different composition and structure. Biophysical factors play a definite role; the non-electrolytic complexes are more capable of permeating the cell membrane than the charged complexes, which is promoted by their higher solubility in lipids.

1. The Role of Chemical and Physicochemical Factors

The formation of stable bonds with nitrogen-containing ligands is characteristic of platinum, which makes it likely that the acido-ligands in the complex undergo nucleophilic substitution by nitrogen-containing DNA bases. However, in order to "reach" the cell DNA, the complexes must react with other biologically active ligands "on the way", namely with proteins, aminoacids, etc. This is the reason for the relation between the chemical reactivity, thermodynamic stability, and kinetic lability of the platinum complexes, on the one hand, and their antitumour activity, on the other. The available data[54] concerning the influence of the complex $[Pt(NH_3Cl)_2]$ on the physicochemical characteristics of DNA show that this interaction proceeds with participation of the aquo-form of the complex as a result of the continuous shift

of the hydrolytic equilibrium

$$[Pt(NH_3Cl)_2] + 2H_2O \rightleftarrows [Pt(NH_3Cl)(NH_3H_2O)]^+ + Cl^- + H_2O \rightleftarrows [Pt(NH_3H_2O)_2]^{2+} + 2Cl^-.$$

There is almost no hydrolysis in the intercellular liquid, where the concentration of Cl^- ions is high (0.103 M). In the cytoplasm and particularly in the nucleus the concentration of Cl^- is much lower (0.004 M); aquo-complexes are formed in the cytoplasm under these conditions and then interact further with the nitrogen-containing DNA bases. A thermodynamic study of all possible equilibria in solutions of platinum complexes and measurement of their kinetic parameters are necessary[12].

2. Thermodynamic Stability of the Platinum Complexes

In aqueous solutions of dichlorodiamineplatinum(II) complexes stepwise hydrolytic and acid–base equilibria obtain:

$$[Pt(NH_3Cl)_2] + H_2O \rightleftarrows [Pt(NH_3Cl)(NH_3H_2O)]^+ + Cl^- ,$$
$$[Pt(NH_3Cl)(NH_3H_2O)]^+ + H_2O \rightleftarrows [Pt(NH_3H_2O)_2]^{2+} + Cl^- ,$$
$$[Pt(NH_3Cl)(NH_3H_2O)]^+ \rightleftarrows [Pt(NH_3Cl)(NH_3OH)] + H^+ ;$$
$$[Pt(NH_3H_2O)_2]^{2+} \rightleftarrows [Pt(NH_3H_2O)(NH_3OH)] + H^+ ;$$
$$[Pt(NH_3H_2O)(NH_3OH)]^+ \rightleftarrows [Pt(NH_3OH)_2] + H^+ .$$

In order to determine the concentrations of all possible equilibrium forms, it is necessary to investigate quantitatively the hydrolytic and acid–base equilibria in solutions of the platinum(II) complexes and to determine the hydrolysis constants K_1 and K_2 and acid dissociation constants K_3, K_4, and K_5, which makes it possible to calculate the contents of all the equilibrium forms existing at the specified concentrations of Cl^- ions and pH values. Such a calculation has been performed for $[PtEnCl_2]$, for which all five equilibrium constants are known; $K_1 = 2.76 \times 10^{-3}$, $K_2 = 1.38 \times 10^{-4}$, $K_3 = 4.0 \times 10^{-8}$, $K_4 = 1.6 \times 10^{-6}$, and $K_5 = 3.1 \times 10^{-8}$. The concentration ratios of the different equilibrium forms in $[PtEnCl_2]$ solutions at pH 7.4 and a Cl^- concentration of 0.103 M in the plasma or 4.8×10^{-3} M in the cell are[54] given below:

	$[PtEnCl_2]$	$[PtEn\,ClH_2O]^+$	$[PtEn(H_2O)_2]^{2+}$	$[PtEn\,ClOH]$	$[PtEnH_2O\,OH]^+$	$[PtEn(OH)_2]$
Plasma	37.3	1	0.00134	1	0.053	0.0033
Cell	1.45	1	0.0345	1	1.38	0.86

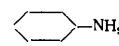
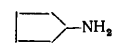
It is seen from the above data that the substance exists in the plasma mainly as the dichlorodiamine complex, while in the cell all the forms (with the exception of the diaquo-complex) are present in comparable amounts. A less detailed approximate calculation has been carried out for $[Pt(NH_3Cl)_2]$ (because K_3 is unknown), from which it follows that the degree of hydrolysis of the complex in the plasma is close to 3%, while the cell contains 42% of the reactive hydrolysis products.

The equilibrium constant corresponding to the elimination of the first chloride ion is usually known for other dichlorodiamineplatinum(II) complexes. The characteristics of the acid properties of the platinum(II) complexes as well as the influence of the σ-donor and π-acceptor properties of the ligands on the acidity of the aquo-complexes have been considered in reviews[55,56].

When concentrated solutions of the platinum(II) complexes are allowed to stand for a long time, polymerisation processes, accompanied by the formation of the complexes $[(NH_3)_2.Pt(OH)_2Pt(NH_3)_2](NO_3)_2$, $\{Pt[(NH_3)_2OH]_3\}(NO_3)_3$, etc. with bridging OH groups, take place[57,58].

For a number of isomeric complexes of the type $[PtA_2Cl_2]$ (A = NH_3 or amines), the hydrolytic stability of the *trans*-isomer is greater than that of the *cis*-isomer. Thus the equilibrium constant for the elimination of the first Cl^- ion in the *trans*-isomer of $[Pt(NH_3)_2Cl_2]$ is 4–5 times smaller and in the *trans*-isomers of $[PtA_2Cl_2]$ (A = methylamine or ethylamine) it is 13–18 times smaller than the corresponding value for the *cis*-isomer[59]. The influence of the strength of binding of the acido-ligand on the antitumour activity of the non-electrolytic platinum(II) *cis*-complexes has already been mentioned. The most stable complexes are the least active: in the $[Pt(AHal)_2]$ (Hal = Cl, Br, or I) series the Pt–Hal bond strength increases and the antitumour activity of the complex falls.

A change in the nature of the amine in the *trans*-position relative to the chloride ions influences the Pt–Cl bond strength in accordance with Chernyaev's principle of *trans*-influence. When NH_3 is replaced by alicyclic ligands, the toxicity is appreciably reduced and the antitumour activity of the complexes increases (see Table 5). Owing to the very poor solubility of the platinum(II) complexes with alicyclic amines, it is not possible to measure their stability constants. A study has therefore been made[60] of the interaction of nickel(II), an electronic analogue of platinum(II), with these amines and the first formation constants β_1 of the nickel complexes were determined (by potentiometric pH titration using a glass electrode) under conditions close to biological conditions (0.150 M NaCl, 37 °C). The basic properties of the ligands increase in the same direction:

L	NH_3		
$\lg\beta_1$	2.80	5.340	6.824
pK_a	9.47	9.97	10.33

It may be that the same behaviour would be observed also for the $[PtL_2Cl_2]$ complexes. In this case the Pt–Cl bond weakens as the Pt–L bond strengthens and the complex becomes less reactive in relation to DNA. However, the use of findings obtained *in vitro* for nickel(II) complexes to explain the differences in the antitumour activities of the platinum(II) complexes *in vivo* must be treated with caution. In order to understand the mechanism of the antitumour activity of the platinum(II) complexes, data for equilibria in the systems containing these compounds together with purines or pyrimidines are particularly necessary. There have been virtually no studies of this kind; one of the causes of this may be the difficulty of the measurements associated with the slowness of the attainment of equilibrium as a consequence of the inertness of the nitrogen-containing platinum(II) complexes. An attempt has been made[61] to estimate the stability constants of the 1 : 1 complexes formed after solutions of mixtures of $[Pt(NH_3H_2O)_2]^{2+}$ with nucleosides (adenosine, guanosine, cytidine, uridine, and thymidine) have been allowed to stand for a long time (4–6 h) at 25 °C in the presence of different Pt : ligand ratios. The quantity ΔA, equal to the difference between the absorbances of the complex and its individual components, has been measured by differential spectroscopy. If it is assumed that only one complex, with the 1 : 1 composition, is formed in the system, then its stability constant K can be found from the equation

$$\frac{b(a-c)}{\Delta A} = \frac{(a-c)}{\Delta\varepsilon} + \frac{1}{K\Delta\varepsilon} ,$$

where a and b are the initial concentrations of the complex and the nucleoside, c is the equilibrium concentration of the complex, and $\Delta\varepsilon$ is the difference between the molar extinction coefficients of the complex and its constituents. By applying the iterative method to the determination of $\Delta\varepsilon$ and c, it is possible to find the optimum values of $\Delta\varepsilon$ and K. $\Delta\varepsilon$ can be determined also directly on the basis of Beer's law. The plot of $b(a-c)/\Delta A = f(a-c)$ is linear, its slope determining the quantity $1/\Delta\varepsilon$ and the intercept on the ordinate axis the quantity $1/K\Delta\varepsilon$.

When $[Pt(NH_3H_2O)_2]^{2+}$ solutions are kept in contact with pyrimidines (uridine and thymidine), no changes are observed in the absorption spectra, which led to the conclusion that there is no interaction. The formation constants of the 1 : 1 complexes with adenosine, guanosine, and cytidine are similar: $pK = 3.5–3.7$. Consequently the reaction of $[Pt(NH_3H_2O)_2]^{2+}$ with the guanosine–cytidine pair is much more probable than with the adenosine–thymine pair: $K_GK_C \cong 10^8$ for the guanosine–cytidine pair and $K_AK_T \cong 10^4$ for the adenosine–thymine pair.

This conclusion is consistent with the experimental finding that $[Pt(NH_3Cl)_2]$ is bound preferentially by DNA enriched in guanosine and cytidine. The selectivity of the reactions of DNA with bases depends on the nature of the metal: copper(II) and silver(I) ions interact preferentially with guanosine, while OsO_4, CH_3Hg(II) and Hg(II) interact preferentially with thymidine[62].

3. Kinetic Lability of the Platinum(II) Complexes

The biological reactivity of the non-electrolytic platinum(II) *cis*- and *trans*-complexes is determined by the kinetics of their hydrolysis and nucleophilic substitution reactions. The kinetic equation for nucleophilic substitution in the platinum(II) complexes has the following form[47]:

$$v = k_1c_c + k_2[L]c_c,$$

where c_c is the concentration of the complex and [L] the concentration of the entering ligand. The first term corresponds to the hydrolytic (solvolytic) pathway and the second to a second-order association reaction with the entering ligand. In the presence of an excess of the latter, we have

$$v = k_{obs}c_c,$$

where $k_{obs} = k_1 + k_2[L]$.

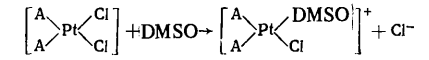
Table 9. Comparison of the kinetic labilities of the *cis*- and *trans*-isomers of $[Pt(NH_3)_2Cl_2]$ at 25 °C.[63–65]

Isomer	Ligand	10^5k_1, s^{-1}	Isomer	Ligand	10^5k_1, s^{-1}
cis-	H_2O	2.5	*cis*-	Cl	0.3
trans-	H_2O	9.8	*trans*-	Cl	7.8
cis-	OH^-	2.5	*cis*-	NH_3	1.0
trans-	OH^-	10.1	*trans*-	NH_3	29.0

In the light of the foregoing, the necessity for a kinetic investigation of the hydrolysis (solvolysis) of the platinum(II) complexes and their reactions with the DNA component is clear. The first process has been studied in fair detail[47]. On the other hand, there are almost no data concerning the rates of reaction of the complex platinum(II) non-electrolytes with the DNA bases and for this reason we shall characterise the kinetics of the second-order reactions using the rates of reaction of the isomeric non-electrolytes with other donor molecules of ions: NH_3, OH^-, Cl^-, etc. Table 9 lists the rate constants for the first-order acid and base hydrolytic reactions and the second-order isotope exchange and nucleophilic substitution reactions with the isomeric platinum(II) non-electrolytes. Evidently the *trans*-isomers are kinetically more labile than the *cis*-isomers. This is usually explained by the greater *trans*-influence of the Cl^- ions compared with the NH_3 molecules.

Numerous studies have been carried out in order to characterise kinetically the *trans*-influence[66,67]. The absence of antitumour activity in the *trans*-isomer can be attributed to its greater lability: on the way to nuclear DNA, the *trans*-isomer enters into rapid and non-specific exchange reactions with a series of nucleophiles. The *cis*-isomer is less labile and is able to reach the tumour cell in an unchanged form and to diffuse through its membrane. In the plasma the concentration of Cl^- ions (0.103 M) is sufficient to suppress the hydrolysis of the complex and only in the cell, where the Cl^- concentration is smaller (0.004 M), is the complex hydrolysed, which is accompanied by the reversible conversion of the aquo-complex into complexes with DNA bases.

The solvolysis of the *cis*-non-electrolytes $[Pt(ACl)_2]$, where A is an alicyclic amine, has been studied in dimethyl sulphoxide[68,69]:



It was established that, on passing from cyclopropyl- to cyclohexyl-amine, the rate of solvolysis falls by a factor of ~2.5; the basic properties of the ligands increase in this direction. The equilibrium constants of the processes

$$cis\text{-}[PtA(DMSO)Cl_2] + A \rightleftharpoons cis\text{-}[PtA_2(DMSO)Cl]^+ + Cl^-,$$
$$[Pt(DMSO)Cl_3]^- + A \rightleftharpoons trans\text{-}[PtA(DMSO)Cl_2] + Cl^-,$$

were determined by a kinetic method (by investigating the rate constants for the forward and reverse reactions).

Kinetic considerations are invoked also to account for the influence of the anion X in $[Pt(AX)_2]$ on the antitumour activity of the *cis*-complex, which decreases in the sequence $Cl^- > Br^- > SCN^- > NO_2^- > I^-$. The rates of certain substitution reactions involving the platinum(II) complexes decrease in approximately the same sequence. For example, the rate constant for the reaction[70]

$$[Pt\,dien\,X]^+ + Py \rightarrow [Pt\,dien\,Py]^{2+} + X^-$$

(dien = diethylenetriamine) diminishes by a factor of 10^6 in the sequence $NO_3^- > H_2O > Cl^- > Br^- > SCN^- > NO_2^-$. Hence one may conclude that the antitumour activity is characteristic of complexes with ligands of moderate lability (Cl^- and Br^-).

One should note that the concepts of the "lability" and "inertness" of the ligand are relative and depend on the charge of the complex and the nature of the remaining ligands and the entering group. Thus the anionic complexes $[PtBr_4]^{2-}$ and $[PtI_4]^{2-}$ are more labile with respect to hydrolysis, isotope exchange, and substitution by NH_3 than $[PtCl_4]^{2-}$:[47]

	10^4K_1, s^{-1}		10^4K_2, litre mol^{-1} s^{-1}
$[PtCl_4]^{2-} + H_2O$	0.39	$[PtCl_4]^{2-} + NH_3$	4.2
$[PtBr_4]^{2-} + H_2O$	1.75	$[PtBr_4]^{2-} + NH_3$	25.0

A more rigorous estimate of the influence of the kinetic lability of the ligand and of the geometrical configuration of the complexes on their biological activity can be obtained after determining the rate constants for the hydrolysis and the interaction with purine and pyrimidine bases of a series of *cis*-isomers $[Pt(NH_3X)_2]$ (X = acido-ligand). One of the few studies of this kind is that of Robins[71], who found that adenine, guanine, and cytosine, their nucleosides, and nucleotides react with $[Pt^{14}C\text{–}EnCl_2]$ (ethylenediamine complex), while thymine and its derivatives do not. Among nucleosides, the reaction is fastest with guanosine and slower with adenosine. This also applies to the reactions with DNA: DNA enriched with deoxyguanosine reacts faster. The presence of the phosphate group in the adenine nucleotides accelerates the interaction.

The absence of antitumour activity in the palladium complex $[Pd(NH_3Cl)_2]$ is due to its kinetic lability; palladium(II) compounds react approximately 10^5 times faster than the analogous platinum(II) complexes[7]. Nickel(II) complexes are still more labile and are therefore relatively unpromising as antitumour preparations. However, one cannot rule out the possibility that the change in the nature of the neutral and acido-ligands in the palladium(II) complexes will reduce their lability and one can then expect that such complexes would be active.

In conformity with the principle of the *trans*-influence, the lability of the ligand is in many respects determined by the nature of the *trans*-ligand. Phosphorus- and sulphur-containing ligands exhibit a strong *trans*-influence and they are responsible for an appreciable increase of the lability of the chlorine bond in *cis*-$[Pt(ACl)_2]$, which is the reason why such complexes are inactive.

Thus comparison of the physicochemical characteristics of the *cis*- and *trans*-isomers of $[Pt(NH_3)_2Cl_2]$ shows that the *cis*-isomer, which exhibits antitumour activity, is kinetically more stable than the *trans*-isomer, but at the same time its thermodynamic stability is lower. It may be that the combination of a moderate lability and a moderate stability of the Pt–Cl bond in the *cis*-isomer ensures the integrity of the complex during its journey to nuclear DNA and its interaction with the latter. While admitting the due importance of these factors, one must nevertheless emphasise that the geometrical correspondence between the *cis*-isomer and the DNA structure exerts a decisive influence on the differences between the antitumour activities of the isomers.

4. Structure Factors and the Interaction with DNA

The structure factors determine the interaction of alkylating antitumour agents (sarcolysine, cyclicphosphoramide, etc.) with DNA. The distance between the chlorine atoms in these molecules is close to 8 Å, which corresponds to the distance between two guanine molecules in two DNA helices[8]. Alkylating agents therefore induce the *interstrand cross-linking* of DNA, which prevents its replication. The structure of $[Pt(NH_3Cl)_2]$ differs from that of alkylating agents, which is reflected in the type of linkage. The distance between the two chlorine in DDP (3.3 Å [72]) approximately corresponds to the distance between the planes of the bases in the DNA helices (3.4 Å), which permits *intrastrand cross-linking* with formation of a chelate complex in which there are two molecules of the nucleoside per platinum(II) atom. The inhibition of the DNA synthesis in the presence of $[Pt(NH_3Cl)_2]$ in a single-strand bacteriophage and the formation of a chelate with the dinucleotide ApA confirm this type of linkage[13,73]. It has also been established that the antitumour activity of DDP is manifested in the proportions of 1 DDP molecule to 1000 DNA base molecules, while interstrand cross-linking requires 20 times as much of the complex[74,75]. For DDP, yet another example of the geometrical correspondence with the DNA structure has been observed. In the crystalline state the distance between the $[Pt(NH_3Cl)_2]$ molecules in the chain structure is 3.47 Å, which permits the combination of the chains of the complex with DNA in which the new double chain contains one nucleoside molecule per platinum(II) atom[76].

The possibility of the interstrand cross-linking of DNA as a result of interaction with DDP also cannot be ruled out[74,75,77], but the majority of investigators give preference to intrastrand cross-linking. They believe that the promising results obtained in the combined chemotherapy with the aid of DDP and alkylating agents are associated with the different mechanisms of their action on DNA.

The problem of which DNA bases interact with DDP and which atoms are involved in such binding has been studied in detail. According to a number of workers, among the purine bases the greatest tendency towards the reaction with DDP is shown by guanine, which is bound to platinum(II) via the $N_{(7)}$ atom[71], while among pyrimidine bases cytosine is most effective, being coordinated via the $N_{(3)}$ atom[78]. In neutral solution thymine does not react with DDP. On this basis, it is suggested that platinum complexes be used to determine the content of the gua-cyt pair in DNA and the sequence of the bases by electron microscopy.

The interaction of DDP and other platinum(II) complexes with DNA containing different amounts of guanine and cytosine has been investigated in detail in a series of studies[79–88] by physicochemical and physical methods (atomic absorption spectroscopy, the fluorescence method, the study of circular dichroism spectra, and the potentiometric determination of the concentration of Cl^- ions). It has been established[87,88] that DDP interacts specifically in the first place with the guanine (gua) of the DNA molecule, forming an intrastrand chelate:

$$[Pt(NH_3Cl)_2] + \text{gua} \rightarrow [Pt(NH_3)_2 N(7)\,\text{gua}\,O(6)]Cl_2 \quad (1).$$

This reaction is accompanied by the liberation of two Cl^- ions per molecule of the contacts, but there is no change of pH. After saturation of the guanine binding sites by the complex, the second mode of binding—the interstrand cross-linking gua $N_{(1)}$–Pt–cyt $N_{(3)}$—is observed in the second stage of the process and is accompanied by the elimination of a proton from the $N_{(1)}H$ group of guanine.

However, this type of binding is non-specific; it obtains also in other platinum(II) complexes without antitumour activity. Apart from the incorporation of the interstrand mechanism, in the second stage of the interaction of DDP with DNA there is a possibility of the formation of an intrastrand chelate with adenine via the $N_{(7)}$ atom and the NH_2 group[85]. This process proceeds via pathways of the type of reaction (1) without the elimination of the proton and with liberation of two Cl^- ions.

It is also believed[87] that DDP initially forms an intrastrand chelate with the DNA guanine, which weakens the cyt–$N_{(1)}$–gua hydrogen bonds, as a result of which a second DDP molecule can be bound to the $N_{(1)}$ atom of guanine. This distorts the initial configuration of the DNA molecule and permits interstrand cross-linking with participation of the $N_{(1)}$ atom of adenine.

The formation of a chelate between DDP and DNA with participation of the $N_{(7)}$ and $O_{(6)}$ atoms of guanine was demonstrated by the investigation of the X-ray electron spectra of the isolated solid platinum complexes of DNA: the ionisation energy of the $N_{(1S)}$ atom of guanine in the series of complexes $[Pt(NH_3Cl)_2]$, *trans*-$[Pt(NH_3)_2Cl_2]$, and $K_2[PtCl_4]$ decreases by 0.5–0.7 eV during their coordination, while the ionisation energy of the $O_{(1S)}$ atom decreases only in the case of the DNA complex with DDP, remaining unaltered in all other cases[80].

In order to examine the interaction of DDP with DNA, a comparative study was made (*in vivo* and *in vitro*) of the reactions of DNA with DDP and other, inactive platinum complexes: *trans*-$[Pt(NH_3)_2Cl_2]$, [Pt dien Cl]Cl, $[Pt(NH_3)_3Cl]Cl$, $K[Pt(C_2H_4)Cl_3]$, $K_2[PtCl_3]$, etc.[89] These complexes also react with DNA but in a different manner. On reaction with DNA, the complexes *trans*-$[Pt(NH_3)_2Cl_2]$ and [Pt dien Cl]Cl split off one Cl^- ion per platinum(II) atom, which indicates their monodentate binding to the central atom. The binding site is again the $N_{(7)}$ atom of guanine[89].

The influence of the platinum(II) complexes on the fluorescence intensity in the DNA–EtdBr system, where EtdBr is ethidium bromide, has been investigated[86]. The triammine complexes [Pt dien Cl]Cl and $[Pt(NH_3)_3Cl]Cl$, which bind to DNA as monodentate species, decrease the fluoresence intensity by only 15–20%; under the same conditions, DDP, $[PtEnCl_2]$, and their aquo-forms, which are capable of chelate formation, exert a much greater influence, reducing the fluorescence intensity by 70%. The inert complexes $[Pt(NH_3)_4]Cl_2$ and $[PtEn_2]Cl_2$ do not react with DNA. The interaction of *trans*-$[Pt(NH_3)_2Cl_2]$ with DNA is interesting: in solutions with an equimolar content of Cl^- ions this substance behaves as a monodentate ligand in relation to DNA, while in the absence of Cl^- ions it greatly reduces the fluorescence intensity and strongly influences the DNA structure. The authors[86] believe that in this case *trans*-$[Pt(NH_3)_2Cl_2]$ forms an unusal chelate with DNA via the $N_{(7)}$ atom of guanine and the oxygen atom of the phosphate group.

The atomic absorption method proved to be promising for the characterisation of the interaction of isomeric non-electrolytes with DNA; it has been observed[90] that the absorption intensity in atomic absorption spectra of the chelate complexes $[Pt(NH_3)_2N_{(7)}guaO_{(6)}]Cl_2$ and $[PtEnN_{(7)}guaO_{(6)}]\cdot Cl_2$ is lower by a factor of 2 than for complexes bound as monodentate species, for example, *trans*-$[Pt(NH_3)_2N_{(7)}guaCl]\cdot Cl$ and [Pt dien $N_{(7)}$gua]Cl_2.[90] Thus the interaction of DDP with DNA is distinguished by the following features:

(1) *In vivo* certain platinum complexes with a labile Cl–Pt–Cl *trans*-coordinate, for example, $K_2[PtCl_4]$, $K[Pt(C_2H_4)Cl_3]$, $K[Pt(NH_3)Cl_3]$, and *trans*-$[Pt(NH_3)_2Cl_2]$, are kinetically unstable in relation to many biologically active ligands (aminoacids and proteins) and do not therefore reach the nuclear DNA, since they react with these substances already in the plasma. In particular, this applies to the complex $K_2[PtCl_4]$, which is more effective in relation to proteins and enzymes than to DNA [87] and differs sharply in its physiological action from DDP; it is bactericidal, highly toxic, and inactive against tumours.

(2) *In vitro* many platinum(II) complexes are capable of reacting with DNA (with the exception of inert tetramine complexes) preferentially as a result of binding to guanine. However, complexes of different structure are formed and differ in the mode of binding. The primary binding of DDP and other *cis*-non-electrolytes leads to the formation of the intrastrand chelate $N_{(7)}guaO_{(6)}$, while *trans*-$[Pt(NH_3)_2Cl_2]$ and triamine complexes are bound as monodentate species via the $N_{(7)}$ atom of guanine. In the concluding report at the IIIrd International Symposium on the Applications of Platinum Complexes in Tumour Chemotherapy Rosenberg[89] emphasised particularly the importance of the formation of this type of chelate for the manifestation of antitumour activity by the complex.

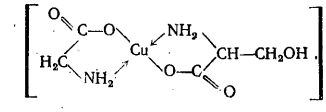
The complex $K_2[PtCl_4]$ binds to DNA via an interstrand mechanism involving the $N_{(1)}$ atom of guanine and the $N_{(3)}$ atom of cytosine, which is accompanied by the elimination of a proton from the $N_{(1)}H$ group. In the solid complex obtained by treating DNA with $K_2[PtCl_4]$ and containing a DNA molecule and two Cl^- ions per platinum atom, interstrand binding via the $N_{(1)}$ atom of adenine and the $N_{(3)}$ atom of thymine as well as monodenate binding via the $N_{(7)}$ or $N_{(3)}$ atoms of guanine and adenine are also postulated.

It follows from the foregoing that the study of the reactions of isomeric non-electrolytes and other platinum complexes with individual DNA bases can throw light on the mechanism of the interaction of these compounds with DNA.

Thus one of the principal causes of the antitumour activity of platinum complexes is inhibition of the replication of DNA. However, this interaction alone cannot ensure the complete destruction of the tumour and its metastases; this requires the operation of additional mechanisms. Such an additional mechanism is the immune system of the organism[13]. The involvement of the immune system is confirmed by the following facts: (1) in mice with grafted Sarcoma 180 and cured with DDP immunity to repeated implantation persists for 11 months; (2) the combination of DDP with an immunostimulant (zymosan) increases the therapeutic effect of the complex or the combination with an immunodepressant (hydrocortisone) lowers the antitumour activity of DDP.[91]

IV. THE ANTITUMOUR ACTIVITIES OF OTHER METAL COMPLEXES

A brief survey of studies on the antitumour activities of metal complexes before Rosenberg's discovery of antiblastoma properties of platinum complexes was given by Cleare[7]. Thus copper, nickel, and cobalt diphthalate complexes proved to be active against leukaemia[92], while iron ascorbate inhibited the growth of Ehrlich carcinosarcoma in mice[93]. The chelate copper complex of dimethylglyoxime $[Cu(DH)_2]$, where DH is the dimethylglyoximate anion, increased the life of animals with Ehrlich ascites tumour and Sarcoma 180 by 200–300%.[94] It has been suggested that coordination masks the hydrophilic oxime group and promotes the permeability of the cell membrane to the complex. An activity has been observed also in the copper(II) chelate complexes of thiosemicarbazones. It has been established[95,96] that the aminoacid complexes of bivalent copper show a definite antitumour activity *in vivo* (against the ascites form of Sarcoma 180) and *in vitro* (against lympholeukaemia L-1210). Mixed complexes with cyclically bound aminoacids (*l*-serine, glycine, *l*-alanine, and *l*-threonine) have been investigated[97] and the syntheses and structure of these compounds have been described[98–100]. They showed a pronounced therapeutic effect on mice with dense tumours of two strains—the mammary gland adenocarcinoma (AK-755) and the cancer of the neck of the uterus (RShM-5); the percentage inhibition of AK-755 was, depending on the compound, the method of injection, and time, 80–90% (on the fifth day after a single injection) and 80–50% (24 h after the end of a five day course). However, the effect is unstable and diminishes 1–2 weeks after the course. The best results were obtained for the complexes with *l*-serine and glycine.



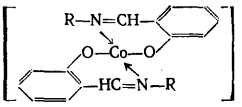
In this case a high percentage inhibition of AK-755 after a single injection persists also on the 19th day. Certain cobalt(III) complexes, namely $[Co(NH_3)_4Cl_2]Cl$ and $[Co(NH_3)_4\cdot(CO_3)]NO_3\cdot\frac{1}{2}H_2O$ retarded the growth of Yoshida sarcoma[101]. There is evidence for the antitumour activity of cyanocobalamin (vitamin B_{12}) [102] and cobalt-protophorphyrin[103].

Complexes of Group VIII elements have been studied in greater detail (after Rosenberg's investigation of the antitumour activities of platinum complexes). Nickel(II) and palladium(II) atoms have the d^7 electronic configuration [d^8, Ed] and are electronic analogues of platinum(II), but the complexes of these elements show a much greater kinetic lability, as can be seen from a comparison of the relative rates of nucleophilic substitution reactions[104]:

Ni (II)	Pd (II)	Pt (II)
$5\cdot10^6$	10^5	1

For these reasons, one can hardly expect antitumour activity of the palladium(II) and nickel(II) complexes; this can also

be said of gold(III) complexes. When the non-electrolytic palladium(II) complexes *cis*-$[Pd(NH_3Cl)_2]$ (the DDP analogue), $[PdEnCl_2]$, $[Pd(NH_3)_2mal]$, [PdEnmal], etc. were tested, no activity against Sarcoma 180 was observed[105]. Nevertheless, one cannot rule out the possibility that palladium(II) can be stabilised by the introduction of cyclic ligands and would then prove active. It may be that this is why the complex $[Pd(dtp)_2]$, where dtp is dimethyl hydrogen thiophosphate, shows some antitumour activity against Walker sarcoma[106]. The cyclic planar cobalt(II) complexes of Schiff bases cause a moderate inhibition of the growth of Walker sarcoma in rats. The best results were observed for the complexes



where R = $(CH_2)_2CH_2OH$ (T/K = 21%) or $C(CH_3)_2CH_2OH$ (T/K = 24%).[107,108] Iridium(III) complexes are inert and inactive, like $(NH_4)_2[IrCl_6]$—an anionic iridium(IV) complex. However, photochemical activation of the latter leads to the formation of the complex *cis*-$[Ir(NH_3)_2Cl_4]$, which has some activity[109].

Rhodium(III) complexes are the most promising. The complexes *trans*-$[RhL_4X_2]Y$, where L = pyridine and its substituted derivatives, and *trans*-$[RhL_2X_2]Y$, where L = 2,2′-bipyridyl, 1,10-phenanthroline, or ethylenediamine (X = Cl, Br, or I; Y = Cl, Br, NO_3, or ClO_4), showed an antibacterial activity and caused the formation of bacterial filaments. In contrast to platinum(II) complexes, this capacity was shown to a greater extent by bromide complexes and not chloride complexes and by complexes with the *trans*-structure and not the *cis*-structure. The introduction of a lipophilic substituent into the pyridine molecule increased and the introduction of a lyophilic substituent decreased the bacteriostatic activity of the complexes. Complexes with pronounced oxidising properties (with less negative half-wave potentials $E_{1/2}$ in polarographic reduction) proved to be more active[110]. The *mer* isomer $[Rh(NH_3)_3Cl_3]$ as well as *trans*-$[RhPy_4Cl_2]Cl$ and *trans*-$[RhEn_2Cl_2]NO_3$ inhibit the growth of Sarcoma 180 and Walker carcinosarcoma (T/C = 17–40%). It has been suggested that under biological conditions the rhodium(III) complexes are reduced to active rhodium(I) complexes.

The antitumour activities of the dimeric rhodium(II) carboxylates of the type $Rh_2(CO_2R)_4$, where CO_2R are acetate, propionate, and butyrate ions, have been studied in detail (in relation to chemical properties)[111,112]. These complexes increased the life of mice with Ehrlich ascites tumour and leukaemia L-1210. The antitumour activity increases in the sequence acetate < propionate < butyrate. In the latter case the life of mice increases by 20%. Rhodium(II) carboxylate complexes inhibit preferentially the DNA synthesis in the tumour both *in vivo* and *in vitro*. However, in contrast to the platinum(II) complexes, they also influence the RNA synthesis (according to data obtained by experiments with tritium-labelled uridine). It has been established that rhodium(II) carboxylates bind preferentially to adenine and its nucleosides and nucleotides. In order to simulate the interaction of the dimeric rhodium(II) carboxylates with DNA, a study was made of their reactions with 5′-AMP, which proceed via an oxidative addition mechanism[113]:

$$[Rh_2(CO_2R)_4] + 2\,(5'\text{-AMP}) \rightarrow [Rh_2(CO_2R)_4(5'\text{-AMP})_2].$$

The changes in the absorption spectra observed in this process are analogous to those which occur on coordination of other N-donor ligands. The formation constants K_1 and K_2 of the rhodium(II) acetate and propionate complexes with 5′-AMP have been determined spectrophotometrically: the propionate complex is approximately twice as stable (K_1 = 4235) than the acetate complex (K_1 = 1893). The stability of the complexes with 5′-ADP and 5′-ATP increases in the same sequence (propionate > acetate > methoxyacetate)[113].

Ruthenium complexes are also capable of interacting with purines and biologically active macromolecules[114,115,116]. The complex $[Ru(NH_3)_5(H_2O)]^{2+}$ is reactive, reacting with purines (guanosine, 5′-GMP, xanthosine, and inosine), which involves coordination via the $N_{(7)}$ atom. In the presence of an excess of ruthenium complex adenine was found to bind via the $N_{(1)}$ atom. The reactions of $[Ru(NH_3)_5(H_2O)]^{2+}$ with DNA occurred similarly. The formation of complexes with DNA and the inhibition of its synthesis by the ruthenium complexes make them potential antitumour agents.

Antitumour activity has been found in compounds of Group III elements: $Ga(NO_3)_3$, which causes 90% inhibition of the development of many tumours, is particularly promising[117]. In contrast to platinum(II) complexes, the gallium(III) compounds accumulate selectively in tumour cells and have a cytotoxic effect on them.

The available data suggest that not only platinum complexes but also other metal complexes, capable of reacting with biologically active molecules, behave as antitumour agents.

Compared with other metal complexes, platinum complexes are stable—they do not undergo extensive hydrolysis and retain their geometric configuration in solution. These complexes served, as it were, as the "starting point" in coordination chemistry: a number of characteristics have been discovered using them—the influence of coordination on the properties of the ligands and the central atom, the mutual influence of ligands, primarily the *trans*-influence, etc. Presumably in the chemotherapy of tumours the platinum complexes will play a similar role and their study will promote the investigation and application of other metal complexes as antitumour agents.

This has been confirmed by the results of the latest studies[118–121], devoted to the search for platinum and other metal complexes and the investigation of the mechanism of their action and their physicochemical properties. Among promising complexes, 4-carboxyphthalato-1,2-diaminocyclohexaneplatinum(II) has been mentioned[122]; promising data have been obtained also for other transition metal complexes[123]. New platinum(II) complexes with pyrimidines[124], adenine, and adenosine[125,126] have been isolated. The presence of oligomers in neutral solutions of diaquodiammineplatinum(II) complexes has been demonstrated by ^{195}Pt NMR.[127] The dependence of the antitumour activity on the structure of the complexes has been analysed[128,129] and the possible mechanisms of their binding to DNA have been examined[130,131].

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Certain Aspects of the Problem of the Pollution of the External and Internal Environment by Lead

V.M.Zatonskaya, F.I.Lobanov, and N.V.Makarov

Studies on the pollution of the biosphere by lead published in recent years are discussed. Numerous sources from which lead can be introduced into the atmosphere and the hydrosphere and, the problems of the contamination of the soil, plants, algae, and animal and human organisms as a consequence of the increased absorption and accumulation of lead are considered. The problem of the chemical forms of lead in the environment, including the internal environment, is described. The bibliography includes 153 references.

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I. INTRODUCTION

The manufacture and consumption of lead in various branches of industry increase continuously; at the same time its release into the biosphere has also increased. Thus 100 000 tonnes of lead were released into the atmosphere in the USA in 1964, which amounted to 10% of the total industrial consumption of lead; the corresponding amount in 1968 was 184 316 tonnes[1]. According to UNESCO data, more than 2.3 million tonnes of lead enter the seas with river water. The atmosphere is also a source of the contamination of the Pacific Ocean by lead. According to Kutyrin's calculations[2], 200 000 tonnes of lead fall on its surface every year.

The number of publications devoted to the problem of the pollution of the environment by lead is large, because lead contaminates various areas—the atmosphere, the hydrosphere, and soils. Many plants grow on soils contaminated with lead accumulate it. The concentration of lead in such lead-enriched plants exceeds the normal content by a factor of 2–100.[3,4] The accumulation of lead by plants merits attention, since not only wild but also cultivated plants, which serve as food products for people, are enriched in lead. Lead can be concentrated at all levels of the aquatic food chain—in both algae and molluscs and fish[5]. Studies in which large amounts of lead were detected in meat and internal organs of domestic animals used as food have been published recently[6,7]. Lead enters the human organism with water and food.

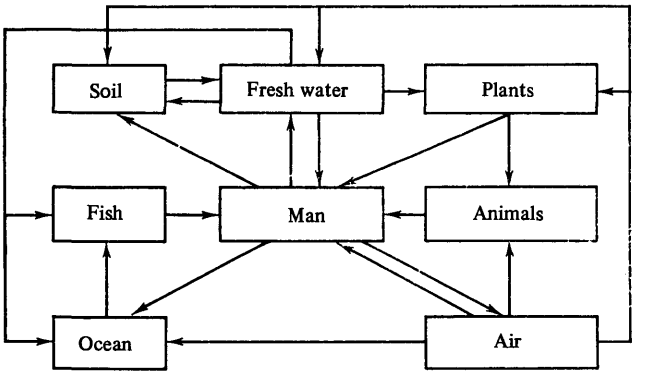
The food chain is not the only source of lead in the human organism. Contamination of air by lead also promotes its penetration into the organism. An increasing number of studies have shown that the main source of lead entering the organism is air contaminated by anti-knocking additives, which contain lead alkyls[8–10]. As a part of organic compounds[11] and also in ointments and cosmetic preparations, lead penetrates through the skin, but apparently only to an insignificant extent[12]. Thus there are two main pathways leading to the chronic action of lead on man—oral and respiratory. The Figure illustrates schematically the migraton of lead in the biosphere.

The global pollution of the environment by lead is indicated by its increased content in polar ice. Thus during the last 25 years the lead content in the snow cover of Greenland has increased by a factor of 400.[13] Lead has also been found in the soil of northern forests remote from industrial regions, where it has been deposited at a rate of 305 grammes per hectare annually[14]. This shows that lead migrates in the environment via the atmosphere in the form of aerosols of lead and its compounds, and the problem of the pollution of the environment by lead has become international, since there are no state boundaries to the movement of atmospheric pollution.

II. LEAD IN THE ATMOSPHERE

1. Sources from which Lead Enters the Atmosphere

The sources of lead in the atmosphere can be divided into natural and anthropogenic. The former include windborne dust, forest fires, volcanic eruptions, sea mist, and plant decomposition products. According to Nriagu[14], the annual amount of lead entering the atmosphere throughout the world from natural sources is 24.5×10^6 kg.



Scheme illustrating the migration of lead in the biosphere.

The anthropogenic sources of lead include lead mines, factories where lead is smelted and lead-containing articles are remelted, factories where various lead compounds are

manufactured, and ferrous and non-ferrous metallurgical plant. The atmosphere is extensively polluted by lead as a result of the combustion of coal, peat, wood, and petroleum fuels used in internal combustion engines, in the combustion of waste, and in the cleaning of tanks and cisterns for the storage of petrol.

The anthropogenic emission of lead amounts to 449×10^6 kg annually[14] and exceeds the natural emission by an order of magnitude. The amount of lead entering the atmosphere on combustion of petrol, which contains anti-knock compounds, amounts to approximately 60% of the total emission from anthropogenic sources.

The total amount of lead distributed in world ecosystems through the atmosphere during the period of civilisation is 20×10^9 kg.[14] A sharp increase of lead emission was observed at the beginning of the 20th century and then in 1923 when anti-knock alkyl-containing derivatives were introduced into petrol.

2. Lead in the Exhaust Gases of Automobiles

One of the principal sources of lead in the environment is the exhaust gases of automobiles and aeroplanes. The waste from automobiles constitutes 57–95% of the pollution of air in many cities of highly developed capitalist countries, more than 40% in Moscow, and 13.3% on average in the USSR.[15] During use, an automobile releases into the environment more than 100 different compounds, the majority having a harmful effect on the environment.

The results of the study of the pollution of air by lead from compounds used as anti-knock agents for internal combustion engines have been published[17]. The authors of this study determined with the aid of ^{203}Pb the amount of lead deposited on the leaves of plants, on the soil, and on grass. It was found that fine aerosol particles (0.01–0.03 μm) are deposited on the surface of plants more readily than large particles (0.2–0.25 μm). Only 10% of the total amount of lead in exhaust gases is deposited on plants 30 m from a motorway with a traffic density of 40000 automobiles per hour; the remaining lead-containing particles remain suspended and are deposited at a much greater distance from the highway.

The anti-knock additives includes mainly alkyl derivatives of lead: $Pb(CH_3)_4$, $Pb(CH_3)_3(C_2H_5)$, $Pb(CH_3)_2(C_2H_5)_2$, and $Pb(C_2H_5)_4$. In the combustion of fuel a significant proportion of the lead bound in organic compounds decomposes and is ejected into the atmosphere in the form of inorganic salts, but a certain amount is ejected unchanged. The results of a study of the levels of organic and inorganic lead compounds in air have been published[18]. By taking samples on filters with a pore diameter of 0.01 μm and using the gas-chromatographic method of analysis, it is possible to determine the concentrations of organic and inorganic compounds of the element. It has been established that most of the lead detected in the atmosphere is present in an inorganic form, while the concentrations of organic lead compounds in air are very low, amounting to 10^2–10^3 μg m^{-3}.

In a review[19] devoted to the problem of the pollution of the atmosphere by tetraethyl-lead (TEL) and tetramethyl-lead (TML) it is noted that their content in the atmosphere is less than 5% of the total amount of lead present. The authors[19] explained this finding by two causes: the fairly rapid photochemical decomposition of these compounds and the presence in the atmosphere of substances accelerating their decomposition. Among these, the most active are NO_x, O_3, atomic oxygen, and the radicals $OH^{\cdot}$, $CO^{\cdot}$, etc., the reactions of alkyl derivatives of lead with these substances being fairly rapid also in the dark. The kinetics and mechanisms of the main homogeneous reactions of TML and TEL in the atmosphere have been investigated[20]. It has been found that the lead alkyls are relatively stable in the dark and have half-lives of 320 and 100 h for TML and TEL respectively in purified dry air. Both compounds are unstable to the action of ultraviolet light and decompose in the light via first-order reactions with photolytic decomposition rate constants of 3.4×10^{-4} min^{-1} for TML and 1.3×10^{-3} min^{-1} for TEL (after subtracting the corresponding values for the dark reactions).

Thus the rate of photolysis of TEL is almost four times greater than that of TML. This is probably why, among lead alkyls, only TML can be detected in the air over our motor highways with a high traffic density, its content amounting to 1–20% of the total concentration of lead in the air[21]. As regards the mechanism of the homogeneous reactions of lead tetra-alkyls, the authors[20] concluded that it is analogous to the mechanism of the hydrocarbon decomposition reactions. The reactions of TML and TEL with O_3, $O^{\cdot}$, and $OH^{\cdot}$ are analogous to the reactions of alkenes, particularly ethylene and propene.

The following mechanism of the reaction of TML with ozone has been proposed[20]:

$$Pb(CH_3)_4 + O_3 \rightarrow (CH_3)_3PbOOH + CH_2O^{\cdot} ,$$

The rate constant for this reaction has been determined as 1.9×10^{-3} $(p.p.m.)^{-1}$ min^{-1}. The rate constant for the reaction of TEL with ozone is 1.6×10^{-2} $(p.p.m.)^{-1}$ min^{-1}. Lead alkyls can react with atomic oxygen either via reaction (1) or via reaction (2).

$$R_4Pb + O^{\cdot} \leftarrow R_3PbO^{\cdot} + R^{\cdot} ; \quad (1)$$

$$R_4Pb + O^{\cdot} \rightarrow R_3PbCH_2^{\cdot} + OH^{\cdot} ;$$

$$R = CH_3 \text{ or } C_2H_5 . \quad (2)$$

The rate constants for the above reactions are 7.0×10^2 and 18.9×10^2 $(p.p.m.)^{-1}$ min^{-1} for TML and TEL respectively[20].

The interaction of $OH^{\cdot}$ radicals with lead tetra-alkyls most probably proceeds via the mechanism

$$R_4Pb + OH^{\cdot} \rightarrow R_2PbCH_2^{\cdot} + H_2O .$$

The rate constants are 13.3×10^3 and 11.7×10^4 $(p.p.m)^{-1} min^{-1}$ for TML and TEL respectively.

According to the data of Harrison and Perry[22], the concentration of lead tetra-alkyls in city air near motorways is on average 0.1 μg m^{-3} and constitutes less than 5% of the total content of lead, which agrees with Baba's results[19].

Between 80 and 100% of lead compounds found in the exhaust gases of automobiles consist of the lead halides $PbBr_2$, $PbCl_2$, PbBrCl, and the α- and β-forms of the double salt $2PbBrCl.NH_4Cl$. The composition and size of the particles in the exhaust gases have been studied in detail[23] using a scanning microscope. It was found that the large particles (>200 μm) contain mainly PbBrCl, $2PbO.PbBrCl$, and insignificant amounts of $PbSO_4$ and $Pb_3(PO_4)_2$; the main lead compound in 2–10 μm particles is PbBrCl. Particles with a diameter >5 μm contain 20–30% Pb, those with a diameter of 1–5 μm contain 50–70% Pb, and only 5% Pb is present in submicroparticles.

More than 90% of the particles in the exhaust gases have dimensions less than 2 μm. Thus, as a consequence of the high degree of dispersion of the particles in the exhaust gases from automobiles, there is a high probability of the penetration of lead into the organism via the respiratory pathway. We may note that the concentration of lead in city air has reached dangerous levels, bearing in mind that 1 litre of petrol contains 200–600 mg of lead, 50–70% of which is ejected into the air with the exhaust gases[24]. The possible ways of combating the pollution of the environment by lead

involve the creation of fundamentally new engines and new catalysts and the use of unleaded petrol. The results of experiments have demonstrated a decrease of the lead content in the parts of cities with a reduced automobile traffic[25].

3. The Lead Content in the Atmosphere and Its Biological Action

Although the views on the mechanism of the absorption of lead via the respiratory pathways are contradictory, it has been suggested that a considerable proportion of the lead breathed in enters the blood through the tracheobronchial system. According to the data in Ref. 21, 35% of the total amount of lead breathed in enters blood.

Results obtained in the inhalation by rats, over 40–60 min, of the aerosol of the exhaust gases from engines working on petrol with added TEL containing the ^{203}Pb isotope have been published[26]. The authors suggest that lead is absorbed by rats mainly through lungs and not through the gastrointestinal tract. It has been noted that lead assimilation processes during inhalation are fairly similar in rats and in men, but there are significant differences in the metabolism of the assimilated lead.

Cantrell et al.[27] caused baboons to inhale Pb_3O_4 dust (particle diameter 3.2 μm) at a concentration of 1.5 μg m^{-3} in the course of 4 h per day for 26 days. It was found that, whereas the initial lead content in the blood was 9.9 μg/100 ml, after 24 h of inhalation it rose to 19, and after two days to 41 μg/100 ml.

Data concerning the concentration of lead in the atmospheric dust of large cities in the industrial centres of Canada exceeding the natural concentrations by a factor of 18–300 have been published[28]. Following the inhalation of 0.1 g of dust with a lead concentration of 1500 μg g^{-1}, which corresponds approximately to its content in the dust of a medium-scale industrial city, man accumulates up to 20 μg of lead. In rural areas the absorption of lead with dust amounts to 5% of its total daily intake (with food, water, and air), while in a large industrial city it amounts to 60%.

People constantly exposed to air containing 4.5 μg m^{-3} of lead (the concentration over large industrial cities) absorb 91 μg of lead in 24 h. Depending on the particle size, the organism retains approximately 30–40% of the lead absorbed in this way, which amounts to 36 μg in 24 h.[29] In Philadelphia the level of lead in the blood of 11 women living in city areas amounted to 29 μg/100 g and more, while the concentration of lead in the city air was 1.7 μg m^{-3}.[25]

In many investigations it has been emphasised that the level of lead in the blood depends on a multiplicity of different factors and not only on the lead content in the atmosphere. Thus a detailed study of the biological action of lead aerosols on the inhabitants of Tokyo has been described[30]. The limiting concentration of lead in the atmosphere was 0.63 μg m^{-3}. The level of lead in the blood varied in the region of 16.8 to 18.7 μg/100 ml depending on the given person's place of residence and occupation. However, a positive correlation between the lead concentration in the blood and its content in the atmosphere has not been established. No correlation has been found either in a study[31] of the biological action of the lead content of the atmosphere on the inhabitants of 7 American cities. However, it has been shown[32] that the lead content in the blood of the inhabitants of Teheran is closely related to street traffic; the lead concentration in the blood increased with age and was higher in cancer patients than in healthy people. In Italy tests were made on the level in the blood of people living in industrial city regions and in the region devoted to the ceramic industry[33]. The average lead contents in the blood were respectively 26.02, 32.21, and 58.06 μg per 100 ml. The lead content in the blood was higher in men than in women and higher in male smokers than in non-smokers. Thus smoking can be regarded as one of the ways whereby lead penetrates into the human organism.

It has been shown[25] that the average level of lead in the blood increases slightly under the influence of air with a lead content of approximately 2 μg m^{-3}; in the presence of this amount of lead in air the lead concentration in the blood of most people is approximately 30 μg/100 ml. It has been calculated[34] that after exposure to an atmosphere containing lead at a concentration of 2 μg m^{-3}, the amount of lead absorbed from respiratory pathways is on average 14 μg per day. The average lead contents in the blood of city inhabitants in different countries are 12.1 μg/100 ml,[35] 25 μg/100 ml,[36] and 43 μg/100 ml.[37]

III. CONTAMINATION OF THE SOIL AND PLANTS BY LEAD

1. Lead in the Soil Near Smelting Plants, Mines, and Industrial Undertakings

The Clark level of lead in the Earth's core is 1.6×10^{-3}%.[38] In the region of abandoned lead amines, smelting plants, and industrial undertakings associated with the production of lead and its compounds, the content of this metal in the soil, particularly in the surface layers, is much higher. Extremely high concentrations of lead (>5000 μg g^{-1}) have been found in the upper layers of soils in direct proximity to industrial undertakings involved in the processing of scrap metal and used batteries and outside the storage areas of factories manufacturing batteries.

It has been shown[39] that the lead content diminishes exponentially with distance from the source of pollution. Analogous data have been quoted in other investigations. Dust and specimens of dirt collected on the surface of the Earth at a distance of 1 km from smelting plants contained 3541 to 5466 μg g^{-1} of lead, whilst at a distance of 2.5 km the content was 397 μg g^{-1}.[40] In many studies devoted to the determination of lead in soil near industrial undertakings its high content was also observed[41–43]. It is noteworthy that the lead concentrations in the soil of open spaces and playing fields remote from industrial undertakings and automobile highways were 800 μg g^{-1} (in 900 soil specimens[44]).

Lead accumulates in the soil not only as a consequence of its contamination by industrial waste, but, as mentioned above, also as a result of the pollution of air by the exhaust gases from motor transport. Near motorways, the concentration of lead in the soil and in the dust covering plants is enhanced. According to Strusinski's results[45], the highest amounts of lead have been detected at a distance of 10 m from the road; with increase of the distance from motorways, the concentration of lead diminishes. It has been shown[46] that lead accumulates on the surface of soils in layers 0–5 cm deep. Specimens taken from rice fields at a distance of 3 to 5 m from a motor highway contained 11–100 μg g^{-1} of lead; in specimens taken at a distance in excess of 3–5 m the Clark level of lead was not exceeded.

The ability of lead to be absorbed by various soils is extremely high. Thus, in a study of the distribution of metal ions between the soil and a solution, it was established[47] that in the pH range 3.5–4.5 the degree of adsorption diminishes in the following sequence: Pb > Cu > Cd ≅ Zn > Ca. The absolute amounts of adsorbed ions increase with the concentration in solution and the adsorption and desorption half-lives are in the range 5–15 s. Since soil is a complex multi-

component system incorporating fungi and enzymes in addition to organic and inorganic ingredients, it is to be expected that lead will influence them. In an experiment designed to investigate the influence of lead on the self-purifying capacity of soils it has been observed[48] that, among all the parameters of the biological activity of the soil, the activity of enzymes is the most sensitive to the action of lead. Lead at a concentration of 100 μg per 100 g of soil suppresses the dehydrogenase activity of the soil to a fairly high extent. In a study of the toxic effect of lead salicylate, acetate, and oxide on soil enzymes it was found that the salicylate causes the greatest inhibition of enzyme activity, while the oxide has the least effect[49], i.e. the most water-soluble compound exerts the greatest influence.

2. Contamination of Plants with Lead

The possibility of the stimulating effect of lead at low concentrations on plants has been pointed out in Soviet studies[50,51], but the problem of the relation between the lead concentrations in the soil and the biological effect has not been solved in the above investigations. In studies of recent years much attention has been devoted to the establishment of a correlation between the amount of lead introduced into the soil and its effect on the development of plants. Thus it has been demonstrated[52] that the introduction of lead acetate into the soil at a concentration of 100 mg kg^{-1} and of lead carbonate at concentrations of 500 and 5000 mg kg^{-1} has a positive effect on the growth and development of Khar'kovskaya-46 wheat. On the other hand, lead acetate at concentrations of 500 and 5000 mg kg^{-1} inhibited the growth of plants. The different effects of lead salts are attributed to the low assimilability of lead carbonate as a consequence of its low solubility and also to the change in the pH of the soil water after the introduction of lead salts. No data were published in the above study[52] concerning the lead content in the plant itself.

It has been stated[53] that the introduction of lead into the soil at concentrations up to 1000 μg g^{-1} does not have any effect on rye and oats sown in sandy loam. A further increase of the lead concentration leads to a sharp decrease of the rate of growth. The introduction of fertilisers does not decrease the harmful effects of lead at its concentrations in excess of 1000 μg g^{-1}.

According to Vinogradov's data[54], the Clark content of lead in plants is 1.0×10^{-4}%. In regions with soils contaminated by industrial waste and automobile transport, lead has been found to have been accumulated by plants. The accumulation of lead by plants grown on soils with its different contents has been investigated[3]. The results showed that potatoes, cabbages, tomatoes, cucumbers, onions, and carrots grown on soils with a lead content of 220–480 mg kg^{-1} contain 2–5 times more lead than the vegetables grown under the same climatic conditions but on soils with a lower lead content (18 mg kg^{-1}). The authors[3] conclude that the lead concentration in vegetables is on average smaller by two orders of magnitude than its concentration in the soil on which they have been grown and that the accumulation of lead by plants on lead-enriched soils compared with that on normal soils differs by a factor not greater than 10.

It has been established[4] that different plants are capable of absorbing different amounts of lead under identical conditions. The minimum amount of lead was found in the seeds of leguminous plants—peas and beans. The maximum amount was found in the leaves of the turnip and egg plant—16.2 and 22.4 mg kg^{-1} respectively. On average, the lead content in the majority of plants was 2–3 mg kg^{-1}. When lead was introduced into the soil in the form of an aqueous solution of its acetate in doses of 50 and 100 mg per kilogram of soil, the leaves of lettuce accumulated 17 and 32 times more lead respectively than in control plants. For the majority of plants, a proportionality has been observed between the lead content in the soil and its accumulation in the plants.

The ability of lettuce to accumulate lead in appreciable amounts has been reported in a study[55] where the species response of lettuce to lead was investigated. Nine species of lettuce were grown by the hydroponic method with addition of lead to the nutrient medium at concentrations of 0.1–50 mg kg^{-1}. It was shown that low concentrations of lead (0.1–0.5 mg kg^{-1}) stimulated the growth of the roots and leaves on the lettuce, particularly in the early stages, while concentrations in excess of 50 mg kg^{-1} significantly inhibited the growth of plants after 4–6 weeks. Differences in the responses of the lettuce species considered, characterised by similar morphological structures, were discovered, which indicates a genetic regulation of the physical mechanisms of the assimilation and transport of lead in plants. It has been suggested that species selection will make it possible to obtain plants with a reduced capacity for the accumulation of lead and hence to reduce to a minimum the risk of the introduction of lead into the organism with food. The important conclusion has been reached[56] that the lead content in pea plants grown in pots with a lead-contaminated soil is correlated with the level of the water-extractable lead and not with its total content in the soil.

As noted above, roadside plants in the vicinity of a highway with intense motor traffic or near industrial undertakings contain much more lead than plants in regions not subjected to the influence of automobile transport and industrial pollution. Thus the lead content in grain cereals grown on lead-contaminated soils is appreciably increased[57]. In the immediate vicinity of a motor highway grass was found to have a maximum lead concentration of 206 mg kg^{-1}.[58]

In the course of a number of years Ocker and coworkers[59–61] investigated the content of mercury, lead, and cadmium in specimens of wheat and rye and in their processing products. It was established that lead is present in the grain in amounts of 0.1–0.2 mg kg^{-1} and is concentrated in its outer layers. The lead content is associated with the region in which the plants are grown and is particularly high in fields located near industrial centres. In the course of the husking of the grain up to 70% of lead is removed; approximately 40% of the lead contained in the grain enters the flour in the milling of the Canadian "durum" wheat. It has been shown[60] that a daily intake of 3 mg of lead by the human organism is harmless to health. It has been pointed out that the permissible lead content in food products is $\leqslant$0.5 mg kg^{-1}. In a number of studies it has been emphasised that, provided that technical instructions as regards the growing and gathering of the crop are adhered to, there is at present no acute risk to the health of people due to the contamination of food products by lead in connection with automobile exhausts.

Studies over a period of many years[62–64] have demonstrated the ability of lichens to accumulate the radioactive isotope ^{210}Pb. Natural breakdown in the ^{226}Ra chain is the source of supply of ^{210}Pb into the biosphere. The long half-life of ^{210}Pb ensures a global distribution of the isotope in the atmosphere and its uniform deposition on the Earth's surface. The ability of lichens to accumulate lead is responsible for the increase of lead concentration in all parts of the chain lichen–deer–man. According to the data of Litver et al.[62], 1 kg of dry lichen contains 7.6×10^{-9} Ci of ^{210}Pb.

There are literature data concerning the ability of fungi to concentrate lead[65,66]. Lead at a concentration of 5.34–80.98 mg kg^{-1} has been detected in the majority of puff-balls collected at a distance of 23–24 m from an automobile highway. The metal concentration in the washed and unwashed fungi was virtually the same, its greatest amount being located in the fungal caps[65]. According to Schnellmann and Opitz[66], the greatest amount of lead is contained in the fungus *Psalliota campestris*—the common mushroom—1.0 mg per kg of dry weight.

3. Lead in Seaweed

Many types of seaweed as well as terrestial plants are able to accumulate heavy metals. It has been established[67] that, in the presence of sufficient illumination, thick growths of certain seaweed contain lead in an amount exceeding 70 g per kilogram of dry mass. Careful washing of seaweed in fresh water removed less than 10% of the bound heavy metals. Exposure of seaweed specimens to dissolved lead salts led to a rapid exchange of the Na^+, Ca^{2+}, and Mg^{2+} ions, which are intracellular cations and are bound to the outer surface of the walls and plasmatic membranes. When seaweed is exposed to lead acetate (lead concentration of 100–500 mg kg^{-1}), extremely high losses of organic material occur, which indicates cell damage[68].

Experiments with natural thickets of seaweed have shown that in the vicinity of industrial waste heavy metals such as lead can accumulate to considerable levels without any apparent physiological harm to the aqueous organisms. It may be that incorporation of heavy metals along the cell wall protects the normal state of the metabolic enzymes and the cell structure. However, no attempt has as yet been made to determine the relative abundance of the physiologically harmless lead within the cell or on its envelope. Plants collected at a site where industrial waste is released contain excess amounts of heavy metals. Thus in its habitat in the bays of the Sea of Japan, where the lead concentration in water is 0.01 mg $litre^{-1}$, the plant *Ulva fenestrata* contains 5.4 times more lead than in a control, uncontaminated bay[69].

The authors explained the increased lead content in seaweed by the affinity of lead for the sulphydryl groups of proteins. It has been noted that changes in the geochemical factors of the medium in a polluted bay led to the adaptation of the water plants to the change in its mineral composition. The slow influence of lead on cell growth as a result of its slow accumulation has also been noted in other investigations. Thus the influence of copper and lead on the growth of pigmentation of seaweed has been studied[70]. Even low lead concentrations tend to reduce the amount of chlorophyll and carotenoid. In addition, the generation of oxygen under illumination is suppressed. However, lead should not be regarded as extremely toxic to seaweed. It has been shown[71] that the accumulation of lead by seaweed and water plants is associated with the pollution of the underlying soil when snow collected from cities with intense motor traffic is disposed of in water basins.

The toxicity of TML in relation to the freshwater alga *Scenedesmus quadricauda* has been investigated[72]. When biologically generated TML from a container with a lead solution at a concentration of 5 mg $litre^{-1}$ is bubbled through a medium containing an alga, the cell growth of the latter is reduced by an amount ranging from 85 to 32%. Cells exposed to the action of lead tend to aggregate. Changes were observed in their fine structure.

IV. LEAD IN THE HYDROSPHERE

According to Chow's data[73], lead compounds are introduced into the oceans with continental water in an average amount of 1.7×10^{10} g annually. The main contribution of lead to the hydrosphere comes from industrial waste water, the precipitation of radioactive deposits, and the use in river transport of motors driven by petroleum fuels. It has been estimated[74] that the lead content in the surface layers of fresh water has increased from prehistoric times up to the present by an amount ranging from 0.5 to 5 μg $litre^{-1}$.

As mentioned in the previous sections, the transport and distribution of lead from various sources takes place mainly through the atmosphere. Large lead-containing particles are deposited along the roads and are responsible for the high level of lead in soils. Aerosols with smaller particles are transported by wind and are dispersed around the terrestial globe. On precipitation of snow and rain, these lead compounds are "washed out" of the layers of the atmosphere and enter the soil and the hydrosphere. Naturally the lead content in rain water is correlated with its local content in air, the intensity of motor traffic, and the degree of industrialisation of the region. According to the results of Drozdova and Machon'ko[75], the average concentration of lead in rain water at 16 points in the European territory of the USSR was 5.5 μg $litre^{-1}$ in 1968–1969. Andren and Lindberg[76] found that the average deposition of lead with rain is 20 g per hectare per month. The lead content in the river waters of South Western France has been determined[77] and it has been noted that it varies from 14.4 to 0.2 μg $litre^{-1}$ and that the precipitation of lead in atmospheric rain is higher than its transport in river water.

1. Lead in Polar Ice

The study of polar snow, frozen layers of which permit the determination of its chronological age, is a reliable means of estimating the anthropogenic contribution of lead to the environment as a function of time. The results of studies of the concentrations of 12 heavy metals, including lead, in the snows of Western Antarctic from 1914 to 1974 have been published[78]. It was found that snow became greatly enriched in lead, cadmium, copper, zinc, and silver as early as 60 years ago and that the enrichment factors found in 1914 were comparable to those determined at the present time. The concentrations of the heavy metals were higher than expected on the basis of their average values for the Earth's core and seawater, the values for lead being 0.018 and 0.04 μg kg^{-1}, depending on the kind of filter used. The authors[78] believe that the sources of the heavy metals in polar snows may be their emission from the surface microlayers of the oceans and from plants as well as human activity. However, they believe that the most probable source is volcanic activity, since the changes in the concentrations of metals with time agree with the historic records of volcanic aerosols. Evidence that volcanic aerosols can reach the Antarctic ice cover had been published previously[79].

The results of the above study[78] agree with those obtained by other workers. Thus, according to Murosumi et al.[80], the lead content in specimens of Antarctic snow after 1916 was 0.01 μg kg^{-1}. In northern Greenland the lead concentration proved to be higher than in the Antarctic. The lead content in the ice layers of Greenland extrapolated to 1753, which corresponds to the beginning of the European industrial revolution, is 0.011 μg kg^{-1}. This concentration exceeds by a factor greater than 25 its natural level. During the period from 1933 to 1965 the metal concentration increased

to 0.20 μg kg^{-1}, which exceeds the natural level by a factor of 500. The authors[80] explain this increase of the lead content in polar ice by the contribution of smelting operations, the combustion of coal, and the use of lead-containing antiknock additives, which began actively in 1940.

Sanak and Lambert[81] investigated the variation of the concentration of ^{210}Pb in the ice cover of the South Pole as a function of the depth from which the specimen was collected. 92 specimens collected from depths down to 18 m were analysed, which showed that between 1920 and 1954 the lead concentration increased. The authors explained this either by a change in the rate of the accumulation of snow or by an increase of the concentration of ^{210}Pb in the snow. Possibly both factors operated simultaneously.

2. Lead in Fresh Water

The concentration of lead in fresh waters depends on the site from which samples are removed, on the time of the year, and on the distance from industrial regions. A review[73] presents the results of the determination of lead in fresh waters. Lead was determined during the period 1956–1975 in 42 sources of water located in different parts of the Earth. It was found that the average lead concentrations in fresh waters vary from 1 to 24 μg $litre^{-1}$ and in the majority of rivers and lakes are in the range 1–10 μg $litre^{-1}$.

Higher amounts of heavy metals are located in the surface microlayer and in the foam generated by wind on the surfaces of rivers and lakes. The foam and the surface microlayers can also be enriched in aliphatic acids, esters, alcohols, chlorinated hydrocarbons, microelements, and organic and inorganic forms of phosphorus, nitrogen and carbon. The enrichment of the foam in heavy metals takes place as a result of the pollution of the surface of water by the metals, the retention of material particles in the surface film and in air bubbles, and the atmospheric contribution.

The foam collected in 1973–1974 at the southern and western coasts of Lake Mendota has been analysed[82]. The foam specimens were collected in plastic cylinders and, after destabilisation in the dark at 4 °C for 24 h by the voltamperometric method, the heavy metal content was determined. It was found that 27–28% of the metal from the destabilised foam is present in the dissolved phase. A considerable proportion of the dissolved metal is bound in complexes with organic substances or is associated with the colloid phase. The average lead concentration in the foam is 2.21 mg $litre^{-1}$. The average enrichment factor in the solid fractions was found to be a maximum for lead (1580), being 800, 235, and 80 for the remaining metals (Cd, Zn, and Cu respectively). It is noteworthy that the surface layers and foam have so far been little investigated from the standpoint of the accumulation of lead and other heavy metals.

At the sites of the disposal of city and industrial waste the lead concentration is appreciably increased and can reach 1000 μg $litre^{-1}$ and more. In connection with the struggle for the protection of the environment, industrial undertakings nowadays have purifying equipment to protect water resources from contamination by waste water. "Rules for the protection of surface water from contamination by waste water", defining the conditions for the disposal of waste water and specifying norms for the quality of water are operative in our country. The limiting permissible concentration (LPC) of lead in reservoirs for sanitary and domestic consumption is 0.1 mg $litre^{-1}$; tetraethyl lead must be absent (within the limits of the most sensitive research method)[83]. The following values of LPC have been established for radioactive isotopes[91]: 1×10^{-7} Ci $litre^{-1}$ for ^{203}Pb; 1×10^{-11} Ci $litre^{-1}$ for ^{210}Pb; 5×10^{-9} Ci $litre^{-1}$ for ^{211}Pb. When waste water is released within the boundaries of any inhabited site, the requirements established as regards the composition and properties of the water in a given body of water must apply to the waste water itself, since in practice one cannot hope for dilution and self-purification[84].

The limiting permissible concentration of lead in drinking water, amounting to 100 μg $litre^{-1}$, has been established by the World Health Organisation (WHO); the same quantity has been adopted as the LPC in the Soviet Union. A limiting level of 50 μg $litre^{-1}$ has been established in the USA and Canada, while in Sweden it is 20 μg $litre^{-1}$. Many investigators suggest that the LPC for lead established by WHO be reduced. Thus it has been proposed[85] that a limiting concentration of lead of 30 μg $litre^{-1}$ be established.

In certain countries where lead pipes are used in the water supply drinking water can contain increased quantities of lead. This applies to regions with soft water giving a weakly acid response in which the solubility of lead is enhanced. The average concentration of lead in such water usually varies in the range 50–100 μg $litre^{-1}$ and in certain cases it reaches ≳300 μg $litre^{-1}$. Cases of an increase of the lead concentration in water to 600 μg $litre^{-1}$ are known; when the lead pipes in the water supply were replaced, the concentration of lead in water fell to 3 μg $litre^{-1}$.[86]

3. Lead in Solid Deposits

The lead contents of solid deposits in rivers, lakes, and seas are various and depend on the geochemical conditions and the anthropogenic contribution. The concentration of lead in the solid deposits removed from various regions near Long Island (USA) varies in the range 200–350 μg $litre^{-1}$.[87] The concentration of lead on the surface of the deposits from the Lake Ontario, amounted to 120–137 mg kg^{-1}.[88]

The distribution of heavy metals in the solid deposits and waters of the Amur Bay has been investigated[89] and the degree of contamination of the deposits in the Golden Horn Bay, where there is a large anthropogenic contribution, has been established. The degree of contamination of the deposits in the latter bay decreases in the sequence Pb > Hg > Cd > Zn > Cu > Cr. The ratio of the average concentrations of the elements in the deposits of the Golden Horn and Amur Bays has been adopted as an index of the contamination of such deposits.

For lead, this quantity amounts to 11.1 (solid deposit) and 1.6 (water near the bottom). The above coefficients show that the lead content in the deposits of the Golden Horn Bay is much higher than the background concentration, which is due to the high sorption capacity of the deposits and the low mobility of the metal in the latter. The local character of the increase of the concentration of heavy elements, associated with the disposal of pollutants in the water of the bay, has been emphasised: the concentrations of the elements in the deposits removed from the mouth of the bay is reduced.

The deposits in Newport Bay (California) were analysed[90] by three independent methods. It was found that the concentrations of zinc and lead increase in the upper layers deposited since 1955, when industrial development began in the catchment area.

The compositions of the solid deposits from different bodies of water are different. In those places where argillaceous rocks predominate, the sorption of ions by clay particles takes place via ion-exchange processes and under the influence of adhesion forces. The overall sorption capacity of clays in relation to heavy metal ions depends on the mineral composition and on the pH of the medium[91]. With increase

of pH, the sorption capacity of clays as a rule increases as a consequence of the formation of stable hydroxo-complexes.

4. Chemical Forms of Lead in the Hydrosphere

The complexity of the behaviour of metals in the hydrosphere is due to the presence in water of a large amount of organic and mineral compounds of abiotic origin and those which are formed in the course of the vital activity of water organisms and as the result of their natural death or mass destruction due to unfavourable conditions. These are nitrogen-containing substances, organic acids, aminoacids, vitamins, hormones, and inorganic salts.

The determination of the overall concentration of trace metals in natural waters in order to establish the degree of their toxicity to water organisms and plants can yield erroneous results. Depending on the chemical form of the metal, water with a high lead concentration can be less toxic than another type of water with a lower lead concentration. The ionic form of lead is more toxic to organisms than lead bound in a complex and the greater the stability of the complex the lower the toxicity. The chemical behaviour of lead in the hydrosphere constitutes a problem which has been little investigated. Problems associated with the form of the chemical compounds of lead contained in the solid deposits have been inadequately studied; it is known that lead is present in the form of such compounds in fresh water and sea water.

The chemical simulation of the nature of the trace metals in water has been carried out[92]. A study was made of the behaviour of heavy metals, including lead, in the presence of inorganic ligands (CO_3^{2-}, SO_4^{2-}, Cl^-, Br^-, F^-, NH_3, PO_4^{3-}, and OH^-) and organic ligands [ethylenediaminetetra-acetic acid (EDTA), citrate ions (Cit), histidine, cysteine, and aspartic acid]. The adsorption of metals on the surface of SiO_2 has been studied. It has been established that at pH < 7.1 lead exists in the form of Pb^{2+} ions; above this pH, lead is present as $PbCO_3$ and hydroxo-species. The sum of lead carbonate and its hydroxo-complexes does not exceed 15%. The complexes with sulphate, chloride, and bromide ions exist in very small amounts. The study of the behaviour of lead in the presence of organic ligands has shown that complete binding in the complex takes place at [EDTA] = 30[Pb]. Appreciable binding of Pb^{2+} by citrate ions takes place when the ligand concentration is more than a factor of 10 greater than that of the metal; thus 30% of lead is bound in the form of complexes at [Cit] = 100[Pb]. The distribution of lead between water and the sorbing surface depends on the accessibility of the latter. With increase of the surface area, the degree of adsorption of metals increases. Copper(II) is most readily adsorbed on SiO_2 and is followed in this respect by lead(II) and mercury(II).

In a deposit–water system lead also exists in different forms. Part of the metal can remain in the intermediate water in the form of free or complex ions and can combine with soluble inorganic and organic substances, can be adsorbed on the surface of the deposits, or can be incorporated in the crystal structure of the latter.

The behaviour of different organic substances and heavy metals in the deposit–sea water system under various oxidation-reduction conditions has been investigated[93]. The authors studied three typical forms of natural solid deposits—clay, silt, sand, and the water above these deposits. The lead content in the specimens of the deposits was 177, 93.6, and 64.8 mg kg^{-1}, while the natural level is 20–50 mg kg^{-1}; the lead content in sea water corresponding to the deposits was 0.10, 0.04, and 0.08 μg m^{-3}. Oxidising conditions were established by reducing the pH from 8.2–8.4 to 7–7.5; reducing conditions were created by increasing the pH from 6.8 to 7–7.5. Under oxidising conditions, the amount of lead liberated from the deposits increased, while under reducing conditions it decreased compared with the natural level of lead in sea water. This can be explained by the formation of an insoluble sulphide. The solubilities of $PbCO_3$ and PbS (the compounds of which it is proposed to monitor), the formation constants of the principal species existing under specific conditions, and their percentage contents relative to the total concentration of soluble lead have been calculated[93]. Experimental data show that the type of deposit (clay, silt, or sand) does not control the direction of migration of the elements, which is regulated by the chemical composition of the water; the oxidising or reducing conditions are a fundamental factor.

V. THE EFFECT OF LEAD ON LIVING ORGANISMS

1. Lead in Animal Organisms

There is virtually no evidence in the literature concerning the biological necessity for lead to maintain the vital activity of an organism with the exception of a few publications. It has been reported[94] that the addition of 1.0–2.5 μg g^{-1} of lead (as the acetate) to a diet lacking this element increased the growth of rats by up to 20%; lead oxide and nitrate showed the same effect. Some data indicate that small amounts of lead have neither a favourable nor an undesirable effect. An experiment in which sheep were fed paper from newspapers and magazines (23% of their rations) in the course of 175 days has been described[95]. The lead contained in the paper accumulated in animal tissues, but histopathological studies with the aid of an electron microscope did not reveal any damage associated with the diet.

However, the majority of investigations on animals have shown that even a slight exposure to lead induces visible changes in the microstructure of the kidneys and the liver, affects the blood circulation, alters the central nervous system, and diminishes the reproductive function[96–98]. The biochemical effect includes the inhibition of the activity of erythrocyte aminolaevulinate dehydratese (ALD), an increased elimination of δ-aminolaevulinic acid (ALA) with urine, and an increased concentration of lead in the blood[99]. The reduction of the activity of ALD entails a disturbance of the synthesis of haem. In addition, lead inhibits the decarboxylases of coproporphyrinogen and uroporphyrinogen.

The inhibiting effect of $PbCl_2$ on the activity of adenosine triphosphatase has been demonstrated[100]. After the introduction of neutral lead acetate in the experimental lead intoxication of rats, an increase of the content of nucleic acid in the liver and in the kidneys was observed. The increase of the DNA and RNA concentration was proportional to the lead dose administered[101]. Lead can be regarded as a weak mutagen, since a slight increase of chromosomal aberrations was observed under the influence of the maximum dose tested (0.05 mg kg^{-1}).[102] It has also been established that lead disturbs the normal replication and genetic processes in the cell at doses much lower than those required for the appearance of signs of toxic activity[103,104].

Data concerning the lead content in the blood together with other factors determining the state of animals have been published in numerous investigations. Thus an increased content of lead in the blood, heart, and aorta of rabbits with atherosclerosis induced by a cholesterol-enriched diet[105] and

an increase of the concentration of lead in the blood of monkeys under the influence of psychological stress[106] have been reported.

It has been demonstrated on experimental animals that a deficiency of certain biogenic elements and vitamins as well as a high content of fats in food increase the toxicity of lead. Enhanced poisoning with lead occur in the presence of an excess or deficiency of protein in the diet. A deficiency of mineral components increases to the greatest extent the toxicity of lead, particularly in the presence of a deficiency of elements such as calcium, phosphorus, iron, zinc, and in certain cases copper[107,108]. A hypothetical mechanism of the enhancement of the toxic effect of lead in the presence of low contents of calcium in the food, based on the hypothesis that the observed retention of lead in the organism is due mainly to the decrease of its excretion and not an increase of its assimilation in the gastrointestinal tract, has been discussed in a review[109]. Other workers[110] arrived at the same conclusion. They did not observe significant differences in the assimilation of ^{203}Pb by rats receiving for two weeks a diet with low and high calcium contents, but in the presence of a deficiency of calcium in the diet a decrease of the excretion of lead and its accumulation in the organs and tissues were observed.

The iron deficiency in anaemia promotes an increased assimilation of lead in the gastrointestinal tract of rats[111], while in a lead-intoxicated embryo the incorporation of iron in liver haem was greatly depressed[112]. A vitamin *E* deficiency in poisoning by lead induces anaemia in rats[113,114]. Like other heavy metals, lead blocks the SH groups of enzymes[11,115].

Wild animals, fish, and birds are constantly subjected to the action of lead in the environment. Cases of acute poisoning of migratory birds by lead are known. Thus the concentration of lead in the kidneys and livers of geese, found in Canada, which were either dead or too weak to fly, proved to be 9.21–102.56 $\mu g\ g^{-1}$.[116]

An interesting method for the determination of lead in the environment has been proposed by Stone et al.[117]. In the course of two weeks, ten-day old Japanese quails received a diet containing 14.8–1223 $\mu g\ g^{-1}$ of lead. With increase in the concentration of lead in the diet, the latter accumulated in the tissues; at the end of the experiment the duodenum, the kidneys, the liver, and the shin-bone contained 16.76, 20.18, 3.8 and 1527.1 $\mu g\ g^{-1}$ respectively. The relation between the lead content in the tissues and in the diet was virtually linear. The results obtained can be used, according to the authors[117], to determine the lead content in the environment by a biological method.

It follows from the literature data that, among domestic animals, horses are most susceptible to lead intoxication[118–120]. The kidneys and liver of horses from North Western Saxony (Federal Republic of Germany) contained 0.4 and 0.9 $\mu g\ g^{-1}$ of lead respectively, which is 2–3 times more than its content in the organs of horses from Poland[120]. To prevent the risk to human health, the authors recommend that the liver and kidneys of horses be declared unsuitable for use in food and that horse meat should always be tested for lead content. Horses in regions polluted by smoke from industrial undertakings producing lead have shown symptoms of poisoning by lead and the organs and tissues of young animals were less contaminated than those of old ones. Analysis showed that hay and fodder grass were contaminated by lead in this region[118].

Attention should be drawn to the possibility of the lead poisoning of cattle grazing along highways with heavy automobile traffic. An increased concentration of lead in the internal organs of cattle, pigs, sheep, and horses has been noted in regions located near the sources of the pollution of the environment by industrial waste and under the conditions of a large consumption of green fodder. On the basis of data concerning the average annual consumption of meat, the average weekly intake of lead by the human organisms has been calculated as 0.006 mg.[119] The meat of 180 cows has been analysed[121] and the average lead content in the fresh meat proved to 0.31 mg kg^{-1}, which is higher than the maximum amounts found previously.

The considerable accumulation of ^{210}Pb in the muscles of deer in the extreme north of the USSR, exceeding its content in the muscle tissue of deer in Finland and Sweden by a factor of 10, has been noted[64]. The accumulation of ^{210}Pb in the bone of deer depends on the age of the animals. Five to six-fold seasonal variations in the content of radioisotopes have been noted—maximum amounts are observed at the beginning of spring and minimal amounts in the autumn; the average ^{210}Pb concentration in the bone of deer proved to be 8.3×10^{-9} Ci kg^{-1} according to the determinations in 1967 to 1968.[64]

It is believed[122] that the prolonged exposure of animals to lead at concentrations up to 25 mg kg^{-1} does not entail a significant intake of the element by the organisms of people utilising food products prepared from the meat or obtained from these animals. A large amount of the lead taken up by animal organisms is deposited in the bones, mainly in an inert form. In the determination of different elements in 20 specimens of the bones of domestic animals lead was found in the concentration range 1.5–8.5 $\mu g\ g^{-1}$.[123]

2. Lead in Aquatic Organisms

The toxic effect of lead on fish, molluscs, etc. depends on factors such as the form of lead, the duration of exposure, the type of water, and the specific features of the aquatic organisms. It has been established[5] that a lead concentration of 0.1–15 mg $litre^{-1}$ is acutely toxic to fish; lead arsenate at a concentration of 17.1 mg $litre^{-1}$ does not harm small fresh water fish in the course of exposure for 1 h, while at a concentration of 25 mg $litre^{-1}$ it leads to the death of the fish in the course of 24 h.

Lead can be biologically concentrated at all levels of the water food chain. The ability of sea organisms to concentrate elements at higher levels than those found in their environment has been known for many years. Lead concentration factors in the sea biosphere have been established[124]; they amount to 700 for seaweed, 40 000 for the phytoplankton, 3000 for the zooplankton, 4000 for molluscs, and 40 for the muscles of molluscs. It has been shown[125] that the lead content in the crude mass of the zooplankton varied from 0.3 to 1.5 $\mu g\ g^{-1}$ in 1972 and from 0.2 to 2.6 $\mu g\ g^{-1}$ in 1974. Approximate lead accumulation coefficients in the zooplankton amounted to 3.5×10^6 (for a lead content of 0.06 $\mu g\ litre^{-1}$ in the water of the Atlantic Ocean) and 8.8×10^4 (for a lead content in the water of 0.003 $\mu g\ litre^{-1}$).

Tissues of the oysters in the Missouri Basin contain 0.77 $\mu g\ g^{-1}$ of lead[126]. The tissues of the oysters and molluscs in the coastal waters of Tasmania contain lead within limits not exceeding the permissible sanitary norms[127]. As in the case of animals, the liver and kidneys of fish accumulate lead selectively[128]. Fish from different lakes in Poland and the Baltic Sea have been analysed[129] for heavy metals. The average level of lead was 0.199 $\mu g\ g^{-1}$ and the highest level (2.64 $\mu g\ g^{-1}$) was found in the beluga. In some investigations it has been noted that the accumulation of heavy metals by fish depends not only on the pollution of water by industrial waste but also on the species of the fish,

their age, and their size. The accumulation of metals is proportional to the length and weight of fish[130]. External tissues (shells, scale, and skin) contain higher concentrations of lead than internal organs, which is due to the partial adsorption of metals from sea water and especially to their release from the organisms in the course of detoxication. Like other heavy metals, lead probably forms complexes of mucous membranes, gills, or body surfaces.

3. Lead in the Human Organism

Food products are one of the main sources of the lead intake in the human organism under normal living conditions and the lead content must be monitored. The lead content in certain dietary products has been determined[131] by atomic-absorption spectrophotometry; the results in μg/100 g, are as follows: 90 in the tissues of the cod, 17 in the crab, 115 in the pig, 104 in the rabbit, 8 in apples, 23 in nuts, 160 in tea, and 30 in coffee. Apart from the pathways discussed previously, lead enters food products from the packing. Thus preserved orange and tomato juice absorbs lead from cans during storage—orange juice to a greater extent than tomato juice[132]. On the basis of the results of the investigation, it is suggested that the maximum permissible lead concentration in preserved fruit and vegetable juices is 0.4 mg litre^{-1}. As a result of contact with metallic caps, carbonated drinks are also contaminated with lead[133]. Lead can migrate from porcelain ware into its contents. It has been established[134] that it is extracted in greatest amounts into a 4% solution of acetic acid (0–3 mg litre^{-1} in 24 h at room temperature).

The lead content in food varies from 200 to 300 μg per 24 h.[29] Approximately 10% of the lead is extracted from food in adult humans in the gastrointestinal tract. Since the degree of absorption of lead by children is much greater than by adults (approximately 50% of the lead in food is assimilated), its daily consumption must not exceed 150 μg.[135] Analogous results have been presented in another communication[136].

Children, particularly embryos and newborn babies, constitute a group particularly susceptible to lead. This observation is associated not only with the unusual assimilation of lead by the child's organism but also with the fact that children can accidentally absorb much more lead than adults. Many instances of the poisoning of children who have eaten lead-based paint have been recorded. The lead content in four specimens of paint has been determined by atomic absorption methods[137] and has been found to be considerable; 5114, 2651, 1630, and 1350 mg kg^{-1}.

Lead enters the bodies of children also with dust and dirt. Day et al.[138] determined the potential risk to the child's body due to the lead contained in school yards, kindergartens, playing fields and city streets. The lead content in samples of dust, sand, and earth has been found by atomic absorption spectroscopy; it varies in the range 570–2130 μg g^{-1}. According to the authors[138], the increased lead content in the blood of city children up to the age of five is due to the intake of lead with street dust. The frequency of lead poisoning among children is directly proportional to the degree of industrialisation of the region and is directly related to the amount of food consumed by children. Protein deficiency in children enhances the toxic effect of lead on the organism and its deposition in tissues. Vitamins *E* and *C* and various preparations containing Ca^{2+}, Cu, Zn, Fe, and Se reduce the toxicity of lead, which can be used in the treatment of poisoning by heavy metals[139]. Numerous studies devoted to lead intoxication in children are also related to the non-specificity of the symptoms, which hinders the diagnosis of the intoxication of children, particularly at an early stage.

As in animal organisms, lead inhibits the activity of the enzyme ALD in the human organism. On the basis of the correlation observed between the level of lead in the blood and the ALD activity, it is suggested that the latter be determined to estimate the level of lead in the blood in mass investigations and in the cases where lead acts at low concentrations[140–142]. Other works[143,144] believe that the determination of Zn-protoporphyrin in the globin fraction which incorporates it in place of haem in the presence of lead is a particularly valuable method; this parameter is better correlated with the degree of damage to the nervous system and the generation of blood than the concentration of lead in the blood. Lead in the human organism interacts with nucleic acids, proteins, and cell membranes[145], accumulating in various organs and tissues. Organic lead compounds accumulate in tissues with a high lipid content, while inorganic compounds accumulate in bones[11]. According to a report[146], the levels of lead in the liver, blood, and bones of human beings not subject to lead intoxication are respectively 0.447, 0.026, and 4.002 mg kg^{-1}.

The role of urbanisation in the deposition of lead is reflected in the results of a study by Grandgean et al.[147]. It was established that the lead content in the bones of the inhabitants of Nubia is ten times lower than in the bones of the inhabitants of Denmark, while the lead content in the teeth of Nubians is thirty times lower than among Danes. Lead is one of the elements detected in dental enamel in different amounts. It proved to be the only element present in food products whose concentration is strongly and directly related to the incidence of caries.

In regions associated with the manufacture of lead, its increased content in hair has been noted[148]. It is suggested that hair be used as an indicator of the pollution of the environment by heavy metals, since these elements remain in hair for a long time after contact with them has ceased[149]. According to the data of the Pan-American Health Organisation, lead concentrations in hair less than 70 μg g^{-1} are nontoxic to man[149].

Complex forming agents such as EDTA, also employed in therapy, are used to diagnose lead intoxication. The concentration of lead is determined from the increase of the urinary excretion of the lead complex of EDTA after the injection of Na_2Ca.EDTA.[150] There have been reports of the effectiveness of the treatment of chronic intoxications with penicillamine, cysteine, and citric acid[151]. It is believed[152] to be useful to employ aqueous solutions of sodium pectate for the prophylaxis and treatment of lead intoxications. The protecting effect of tannic acid has been reported[153].

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It follows from the data presented that lead is a complex pollutant of the environment entering the organism via different pathways. Bearing in mind the ability of lead to accumulate and the large number of sources of lead in the environment, its danger is evident. On the basis of the latest studies, many investigators suggest that the limiting permissible amounts lead established previously be reduced. Thus it has been suggested that the PLC of lead in drinking water be set at 30 μg litre^{-1};[85] for children, the authors[28] propose a norm not exceeding 1 μg m^{-3} of lead in air or 50 μg g^{-1} in dust. A norm of 40 μg/100 ml of lead in the blood has been suggested[29] as more acceptable than the previous norm of 80 μg/100 ml adopted at the XVIth Combined Committee of FAO/WHO experts on food additives.

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Emulsion Polymerisation of Non-polar Monomers (Development of Ideas on Kinetics and Topochemistry)

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The kinetics, the topochemistry, and the mechanism of the emulsion polymerisation of non-polar monomers are discussed in the light of results obtained during the past decade. The part played by components of the system, features of the primary reactions, and the theory of emulsion polymerisation are considered. A list of 114 references is included.

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I. INTRODUCTION

Emulsion polymerisation is widespread, technically convenient for the production of monomers, and characterised by several specific features. In its common variants the monomer is dispersed in water, but the polymer is obtained as a latex. All the advantages (and disadvantages) of emulsion polymerisation are due to the heterogeneity of the system, and the possibility of localising the primary reactions in different zones. Improvement of the technology of emulsion polymerisation—the possibility of controlling the structure and working properties of the resulting polymers—is determined by the level to which a general theory has been developed to give a correct interpretation of the kinetic and topochemical features. The difficulty of establishing such a theory is due firstly to the multiphase character of the emulsion system and secondly to the multiplicity of parameters governing the mechanism and kinetics. This diversity is due not only to differences in reactivity of the reactants in specific systems but also to differences in their distribution between the phases. All this complicates the establishment of local zones in which the primary steps take place, as well as the determination of reactant concentrations in these zones, so that kinetic description of an emulsion process becomes difficult.

Thus one of the main problems in a theory of emulsion polymerisation is to establish the sites at which the primary reactions occur and to determine the local reactant concentrations at these sites. It must be noted that a given primary reaction can take place in more than one local zone. Finding a theoretical basis for the presence of local zones, their number, and the distribution of reactants among them, establishing their reactivity as a function of their location—these are the chief tasks of a theory of emulsion polymerisation.

At the present time the greatest certainty has been achieved for the emulsion polymerisation of non-polar monomers, sparingly soluble in water, in the presence of ionogenic emulsifiers and water-soluble initiators. However, existing theories do not give a complete explanation even for this comparatively narrow range of emulsion processes. The new experimental results continually appearing undoubtedly broaden our views and deepen our understanding of the processes occurring in complicated emulsion systems.

The present Review will cover mainly research results published during the past 8–10 years and relating essentially to the emulsion polymerisation of non-polar monomers. Special attention will be paid to work which has not been subjected to detailed consideration in the review literature or has not been discussed at all. Detailed analysis of papers on the emulsion polymerisation of polar monomers will be found in Eliseeva's reviews[1,2].

Before surveying the most recent work on emulsion polymerisation we shall consider briefly existing views based on earlier investigations, as well as some of the main directions in which they have been refined and elaborated.

II. QUALITATIVE PICTURE OF EMULSION POLYMERISATION AND THE SMITH–EWART THEORY

We shall consider the most typical emulsion systems, in which polymerisation takes place by a radical mechanism in the presence of micelle-forming surface-active compounds; the dispersion medium is water, while the disperse phase is a non-polar monomer sparingly soluble in water.

The main principles underlying the technology of emulsion polymerisation in such systems were already known at the beginning of the century[3–5], but ideas on its mechanism were remote from present-day views. It was assumed that polymerisation occurred in drops of the emulsion. Fikentscher[6] was the first to abandon this view and to suggest that polymerisation takes place in the aqueous phase. Later more complete qualitative ideas on the emulsion polymerisation of non-polar monomers were developed[7,8] and supplemented independently[9,10]. We note below only the main principles that follow from this work.

1. Emulsion polymerisation is the usual radical process of polymerisation, the explanation of whose features is that the sites of reaction—micelles and polymer–monomer particles—are discrete volumes.

2. In the initial stage the emulsion system comprises a mixture of micelles of the emulsifier, polymer–monomer particles, and large drops of the monomer.

3. Polymerisation begins only in micelles, which are then converted into polymer–monomer particles, whereas drops of the monomer, in which the process hardly develops, serve

merely as a source of the monomer. Diffusion of the monomer from the drops into the polymer–monomer particles is not rate-determining, so that an equilibrium concentration of the monomer is established in the polymer–monomer particles, which is maintained as long as drops exist.

On the basis of these ideas Smith and Ewart[11] developed a quantitative theory of the emulsion polymerisation of non-polar monomers (more precisely the theory of the emulsion polymerisation of styrene by persulphate in the presence of ionogenic surface-active agents), which was then extended to other systems. Their work, published in 1948, was a most important event in the investigation of emulsion polymerisation, and remains so even to the present time. Hardly any contribution to a quantitative theory of emulsion polymerisation can avoid referring to this work.

Using the principle of quasi-stationarity Smith and Ewart suggested several solutions for the kinetic equation of emulsion polymerisation. The condition of quasi-stationarity for N_n particles containing n radicals can in general be written

$$N_{n-1}(R_i/N) + N_{n+1}k_0a(n+1)/v + N_{n+2}k_t(n+2)(n+1)/v = N_n(R_i/N) + \\ + N_nk_0an/v + N_nk_tn(n-1)v, \quad (1)$$

where R_i is the overall rate of entry of radicals into all N particles (the total number of particles in unit volume), v the volume of a particle, n/v the concentration of free radicals in a particle, a the surface area of a particle, k_0 the rate constant of escape of radicals from a particle, and k_t the rate constant of termination. Thus the left-hand and right-hand sides of Eqn.(1) comprise terms describing respectively the disappearance and the appearance of particles containing n radicals. Smith and Ewart examined three cases.

1. The condition $n \leqslant 1$ corresponds to a high rate of escape of radicals from particles or a small proportion of particles containing a radical. The total number of radicals $R = N_1$, and Eqn.(1) becomes

$$N_1k_0a/v = N_0R_i/N. \quad (2)$$

Since $N_0 \cong N$, we have

$$R \approx N_1 \approx R_iv/k_0a$$

and

$$-\mathrm{d}[M]/\mathrm{d}t = k_{gr}[M](R_iv/k_0a) \quad (3)$$

or

$$-\mathrm{d}[M]/\mathrm{d}t = k_{gr}[M]V_pc_r, \quad (4)$$

where k_{gr} is the chain growth constant, V_p the total volume of particles, c_r the total concentration of radicals in the particles, and [M] the concentration of the monomer in a particle. Thus the rate of emulsion polymerisation is proportional to the total volume of particles. However, this case is seldom realised in practice, and does not find wide experimental support.

2. When $n = \frac{1}{2}$, the rate of escape of radicals from particles is small, but the rate of chain termination is high. As a consequence a polymer–monomer particle can contain at most one radical, and each subsequent radical entering the particle causes the instantaneous recombination of two radicals. As a result, only half the particles contain a radical. In view of the assumptions made, the total number of radicals should be $\frac{1}{2}N$. Hence we obtain an equation in which the rate of emulsion polymerisation is proportional to the number of particles:

$$-\mathrm{d}[M]/\mathrm{d}t = k_{gr}[M]nN. \quad (5)$$

This conclusion is confirmed by numerous experimental results.

3. The case in which $n \gg 1$ is comparatively trivial and is described by relations characteristic of normal radical polymerisation in homogeneous systems. Equation (1) becomes

$$R_i/N = 2k_t(n^2/v), \quad (6)$$

whence after finding n we obtain

$$-\mathrm{d}[M]/dt = k_{gr}[M](V_pR_i/2k_t)^{1/2}, \quad (7)$$

i.e. the rate of emulsion polymerisation depends solely on the total volume of particles and is independent of their number.

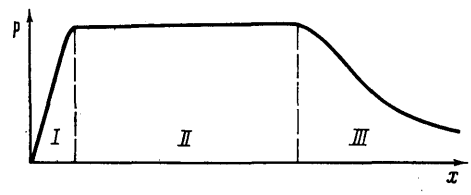


Figure 1. Dependence of rate of emulsion polymerisation on degree of conversion x of monomer into polymer.

The second case is especially interesting, being most often realised in practice and reflecting the features of emulsion polymerisation (for this reason the Smith–Ewart theory is often identified with this case). The qualitative picture and the quantitative theory provide an explanation of the kinetics. The rate curve for non-polar monomers comprises three segments (Fig.1): a comparatively short segment (I), corresponding to an increasing rate of polymerisation R_p, is followed by segment (II), with a constant rate, and segment (III), along which the rate decreases. On the basis of these views section (I), often termed the micellar stage of emulsion polymerisation, can be attributed to formation (nucleation) of polymer–monomer particles and increase in their number. After the micellar soap adsorbed on the particles has disappeared, no new particles are formed, and the R_p remains unchanged along the steady-state segment (II), as all the parameters (k_{gr}, n, N, [M]) are constant. After the monomer drops have disappeared, stage (III) begins, when all the monomer is present in polymer–monomer particles, and the rate of polymerisation falls owing to decrease in the concentration [M] in the particles.

Equation (5) thus describes the steady-state region of emulsion polymerisation, which continues as far as 50–70% conversion depending on the type of monomer. In essence it involves all the kinetic parameters—concentrations of reactants (monomer, initiator, emulsifier) and constants of primary reactions—although only k_{gr} and [M] appear explicitly. The remaining concentrations and constants are included in the parameter N, which according to the Smith–Ewart theory is given by the formula

$$N = k(R_i/\mu)^{2/5}(S_0[E])^{3/5}, \quad (8)$$

in which μ is the rate of increase in volume of the polymeric particle, S_0 the area occupied by 1 g of emulsifier, [E] the concentration of the emulsifier, and k a constant (varying between 0.37 and 0.53). It is evident that the number of particles depends on the rate of initiation, and hence on the initiation constant and the initiator concentration, as well as the emulsifier concentration. The somewhat unusual powers

to which the emulsifier concentration and the rate of initiation are raised are explained by the circumstance that, with a constant rate of increase in particle volume, the total particle surface should increase with time to the power $\frac{5}{3}$.

Equation (8) can be deduced on the postulate that all free radicals formed in the aqueous phase are captured by micelles, when

$$dN/dt = R_i, \tag{9}$$

The change in volume of a particle in the interval between time τ and t

$$v_{\tau t} = \mu(t-\tau) \tag{10}$$

is accompanied by the change in particle surface

$$a_{\tau t} = \theta(t-\tau)^{2/3}, \tag{11}$$

where

$$\theta = [(4\pi)^{1/3}/3\mu]^{2/3}. \tag{12}$$

The total surface area of all the particles will then vary in conformity with the equation

$$A_p = R_i\theta\int_0^t (t-\tau)^{2/3}\,dt = \frac{3}{5}R_i\theta t^{5/3}. \tag{13}$$

Since $A_p = S_0[E]$ at the instant t_1 of disappearance of free soap or completion of formation of particles, we can write

$$t_1 = (5S_0[E]/3R_i\theta)^{3/5}. \tag{14}$$

Hence the number of particles

$$N = R_i t_1 = R_i^{2/5}(5S_0[E]/3\theta)^{3/5} = 0.53(R_i/\mu)^{2/5}(S_0[E])^{3/5}. \tag{15}$$

It can readily be shown that, in the alternative case in which the radicals formed are captured also by particles attached to existing micelles, the formula for the number of particles will be similar but with a rather smaller value (0.37) for k.

It is noteworthy that the initiator concentration and hence the rate of initiation behave rather unusually in emulsion polymerisation. Primarily they affect the number of particles, the time of formation of which depends on the rate of disappearance of the micellar soap. After the disappearance of micelles no new particles are formed, and the rate of initiation ceases to influence the overall rate of emulsion polymerisation. Thus addition of a fresh portion of initiator in the second stage does not increase the rate of polymerisation, since the number of radicals in polymer–monomer particles cannot then change.

The termination constant k_t does not occur in the kinetic equation, since in the classic form (with $n = 0.5$) it does not limit the processes governing the lifetime of radicals and their number in a particle. If, however, it is postulated that two or more radicals may remain in a particle, this constant will play a decisive role, and its influence on n can be represented by the equation[12]

$$n = {}^4/_3 r^3\pi N_A w_i^{1/2}/k_t^{1/2}, \tag{16}$$

in which r is the particle radius and w_i the rate of initiation. In this case great importance will attach to the viscosity of the polymer–monomer particles, which is apparent in the Trommsdorff effect (increase in rate of polymerisation and molecular mass of polymer due to a decreased termination constant in viscous media). Incidentally, this effect cannot legitimately be used to explain high rates and molecular masses of polymers during emulsion polymerisation on the basis of Smith and Ewart's classic concepts: if we postulate the residence of more than one radical in a polymer–monomer particle, we thereby indicate the possibility of departures from the Smith–Ewart theory.

Publication of the theory was later followed by papers[13–15] discussing such deviations, which still continue to appear with considerations of other problems of emulsion polymerisation. For example, the possibility is examined that colloid-chemical parameters of an emulsion system may influence the constants of the primary reactions, the mechanism of formation and the morphology of the polymeric particles, etc.

To avoid becoming involved in the vast factual material and to minimise confusion in its presentation, we shall attempt to analyse the accumulated experimental results by considering in succession the parameters governing the kinetics and the topochemistry of emulsion polymerisation.

Initially we shall examine the concentration parameters [M], n, and N, analysing the reasons for their variation within certain limits and the topochemical consequences of these variations, after which we shall consider the constants of the primary reactions.

III. NUMBER OF PARTICLES IN EMULSION SYSTEM DURING POLYMERISATION

We shall consider the number of particles in the system, and also the other parameters, primarily in relation to the second stage, which is characterised by a constant rate of polymerisation. This is the most interesting stage from the point of view of theory; it usually extends from 5–10% to 50–70% conversion depending on the type of monomer and the temperature. In order that the rate should become constant, of course, the parameters in Eqn.(5) should also remain constant at this stage.

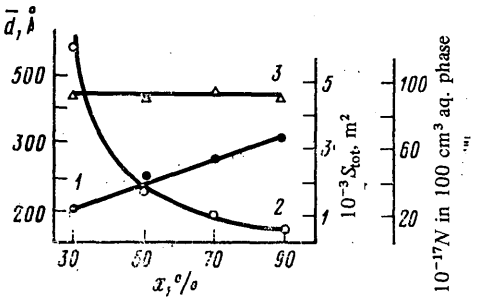


Figure 2. Effect of degree of conversion of styrene[21] on: 1) particle diameter $\bar{d}$; 2) number N of particles; 3) total particle surface S_{tot}.

Constancy of N has indeed been demonstrated in many cases[11,16], as indicated by comparatively recent results for emulsion systems differing from those investigated by Smith and Ewart. For example, in the polymerisation of styrene initiated by the oil-soluble azoisobutyronitrile, N remains constant throughout stage (II).[17] Constancy of the number of particles has also been established[18] in the emulsion polymerisation of styrene in the presence of a mixture of an ionogenic and a non-ionogenic surface-active agent. Unchangeability of the number of particles during stage (II) has been established[19,20] for such an atypical case as the emulsion polymerisation of styrene on potassium peroxodisulphate in the

absence of an emulsifier. Here stabilisation of polymer–monomer particles is achieved by charged SO_4^- end-groups of macromolecules formed by dissociation of the persulphate, and polymerisation is initiated by radical-anions. We shall discuss this work[18–20] in greater detail in connection with the structure of polymer–monomer particles.

However, besides data consistent with the ideas of Smith and Ewart, quite a few results are known that indicate change in the number of particles during the second stage of emulsion polymerisation. First to give a theoretical basis to such phenomena was Medvedev[21], who suggested that adsorbed layers on the surface of latex particles retain in some measure their capacity for interphase exchange among themselves, with a consequent interdependence of polymerisation processes occurring in different proton–monomer particles, so that emulsion polymerisation can be regarded as a quasi-homogeneous process. Medvedev supports this hypothesis with data on the variation in the number of particles, their total surface, and their diameter at various degrees of conversion of styrene and methyl methacrylate[21]. Fig. 2 shows that N falls rapidly with extent of polymerisation, whereas the total particle surface remains constant.

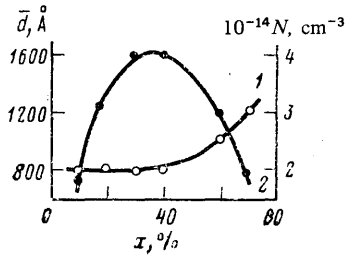


Figure 3. Influence of conversion (0.026 M Alkamon DS in aqueous phase + 0.01 M cumene hydroperoxide in styrene with ratio of monomer to water 1 : 7 at pH 3 and 60 °C [22]) on 1) particle diameter; 2) number of particles.

The Reviewers have also observed[22] variation in the number of polymer–monomer particles during the emulsion polymerisation of styrene, initiated by cumene hydroperoxide in the presence of a cation-active surface-active agent—Alkamon DS $\{C_{12-18}H_{25-37}.O.CH_2.N^+(C_2H_5)_2.CH_3\}CH_3SO_4^-$—although the dependence of N on degree of conversion was more complicated (Fig. 3). However, even in this case the total particle surface remained unchanged after a maximum value had been reached. The increase in the number of polymer–monomer particles until 30% conversion is reached in this sytem can be explained by the very high concentration of emulsifier and extension of the micellar stage to this conversion. The possibility of retaining the micellar soap until high monomer conversions are reached has also been mentioned[23].

The above results show that in several cases Smith and Ewart's postulate that latex particles are discrete is not confirmed. It has therefore been suggested that adsorbed films of emulsifier molecules are the chief site of the primary reactions in emulsion polymerisation. The occurrence of interphase exchange interaction between separate polymer–monomer particles permits the processes to be averaged with respect to the main parameter—the total quantity of soap in the system—and the kinetic scheme to be based on the usual set of reactions of radical polymerisation with reactant concentrations related to the volume of adsorbed films of such particles. In the light of these ideas Medvedev suggested kinetic equations which did not contain the number of particles. For example, with a water-soluble initiator the rate of emulsion polymerisation is given by

$$R_p = k_{gr}[I]^{1/2}[E]^{1/2}[M]^0. \qquad (17)$$

In individual cases Medvedev's theory provides a satisfactory description of qualitative and quantitative aspects of emulsion polymerisation. However, it can hardly be regarded as a more general approach to an explanation and description than is the Smith–Ewart theory, since his conclusions are based mainly on experiments undertaken in the presence of high concentrations of emulsifier and initiator, i.e. under conditions of formation in the early stages of a very large number of particles, which may flocculate because of the rapidly increasing adsorption unsaturation of the system. Similar phenomena can probably take place when the surface-active agent has an inadequate stabilising affect or with a low rate of adsorption of emulsifier on the rapidly formed surface, as occurs in the polymerisation of polar monomers[24]. Furthermore, Medvedev's suggested interphase exchange does not agree well with such a fact as emulsion polymerisation on long-lived radicals in the case of radiation initiation, followed by postpolymerisation after irradiation has ceased[25,26].

Thus Medvedev's theory is not capable of describing the whole variety of phenomena involved in emulsion polymerisation, although it well supplements the Smith–Ewart theory and can justifiably be applied if its limits are intelligently defined. However, it must be stressed that the concept of the discreteness of latex particles in the emulsion polymerisation of non-polar monomers, which usually give well stabilised particles, is more general. For this reason kinetic ideas based on the number of particles in an emulsion system and the number of radicals in them are probably more fertile, and continue to evolve at the present time.

IV. NUMBER OF FREE RADICALS IN A POLYMER–MONOMER PARTICLE

As already mentioned, a single polymer–monomer particle can in principle contain more than one free radical, which is inconsistent with the views of Smith and Ewart. As early as 1957 a theoretical basis was given to such a possibility by Stockmeyer[13], who calculated that such a particle of diameter exceeding 1000 Å can contain several radicals: i.e. the combination of a large particle volume and a high viscosity (with equilibrium swelling at 50 °C the concentration of styrene polymer in a polymer–monomer particle is 43%) makes the presence of several radicals in a particle possible because of the diminished probability of their termination. Subsequently van der Hoff[14], using formula (5) to calculate from data on the emulsion polymerisation of styrene in the presence of cumene hydroperoxide the number of radicals in a polymer–monomer particle as a function of its diameter, showed that even for comparatively small particle diameters considerable departures from $n = \frac{1}{2}$ are possible (Fig. 4).

Since the diameter and the viscosity of a particle (in stage III) increase during polymerisation, the number of radicals in a particle should also increase. Thus a similar calculation for the emulsion polymerisation of styrene has shown[27] that, although the number of radicals does not change very greatly (from 0.5 to 1.0) in the steady state, it rises rapidly after the disappearance of drops of the monomer (stage III) because of a rapid increase in viscosity

in the particle (Fig.5). Similar calculations have been made by other workers[28].

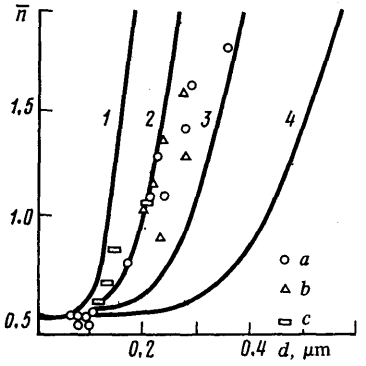


Figure 4. Mean number of radicals in a particle $\bar{n}$ as a function of particle diameter[14] indicated by experimental points for: *a*) $K_2S_2O_8$ at 50 °C; *b*) $K_2S_2O_8$ at 40 °C; *c*) cumene hydroperoxide at 50 °C. The curves have been calculated for different values of lg $[fk_d(I)/k_t]$ (k_d is the decomposition constant of the initiator and f the efficiency of initiation[33]): 1) −12; 2) −13; 3) −14; 4) −15.

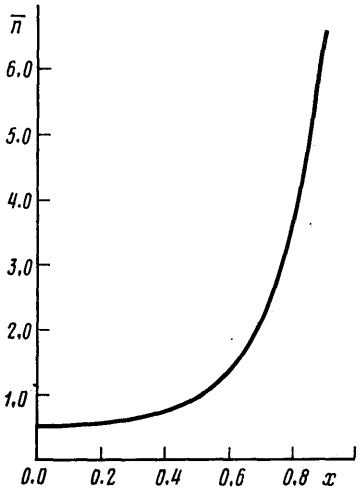


Figure 5. Theoretical dependence[27] of mean number of radicals in a particle $\bar{n}$ on conversion x.

In an investigation of the emulsion polymerisation of styrene (0.01 M) in the presence of cumene hydroperoxide and cation-active surface-active agents (0.026 M Alkamons in aqueous phase, with a 1:7 monomer–water phase ratio at 60 °C) the Reviewers have also shown[12] the possibility of finding several radicals in a single polymer–monomer particle (Table 1), with n dependent not only on particle size but also on rate of initiation. The specific action of the emulsifier made it possible, by varying the pH of the aqueous phase, to increase particle diameter with simultaneous increase in rate of initiation of polymerisation. If a particle contains several radicals, the influence of rate of initiation on n can be described by Eqn.(16).

Table 1. Influence of particle diameter d and rate of initiation w_i on number of radicals n in a polymer–monomer particle during the emulsion polymerisation of styrene[12].

pH	10^3R_p, M (in styrene) s^{-1}	10^8w_i,	$10^{-14}N$, cm^{-3}	$\bar{d}$, Å	n
3	1,62	6,60	1,02	1200	1,61
5	1,91	9,16	0,53	1500	3,27
7	1,02	2,00	0,41	1620	2,22
9	0,70	1,17	0,30	1800	2,12
11	1,40	6,34	0,17	2200	7,47
12	1,92	10,70	0,13	2400	13,4

Thus examination of yet another fundamental parameter of emulsion polymerisation indicates additional limitations on the applicability of the Smith–Ewart theory, associated with the diameter of the latex particles. The theory is fully applicable only to particles of diameter <1000 Å. Nevertheless, Eqn.(5) corrected for the number of radicals describes satisfactorily the steady stage even in the presence of larger particles (for n changes little during stage II), as the rate of initiation remains almost constant[29]).

We note in conclusion that theoretical calculations on the number of free radicals in a polymer–monomer particle are considerably complicated by the possibility of their escape from the latter. This problem is examined in some details in a recent review[30], which notes that the desorption and readsorption of radicals by particles are especially significant in the emulsion polymerisation of polar monomers such as vinyl acetate and chloride, whereas they have little kinetic influence on that of non-polar monomers, e.g. styrene.

V. CONCENTRATION OF MONOMER IN A POLYMER–MONOMER PARTICLE

Consideration of the concentration of the monomer in a polymer–monomer particle—an important parameter of emulsion polymerisation—poses several questions of fundamental significance and widely discussed during recent years—(i) what the concentration is and whether it is an equilibrium value, (ii) whether diffusion of monomer from drops into particles influences establishment of the concentration, (iii) whether the concentration is constant during polymerisation, and (iv) the distribution of the monomer within the particle—to the first three of which the Smith–Ewart theory gives unambiguous answers. The last question, which is ignored in the classical theory, is especially important, since it concerns not only the kinetic aspect of emulsion polymerisation but also the mechanism of formation and the morphology of a latex particle. All the questions certainly apply to the steady state of emulsion polymerisation, since answers to them are given primarily to explain the existence of this second stage. Since Smith and Ewart's ideas have been outlined above, we shall consider only Morton's physical interpretation of the monomer concentration in a particle[31].

The equilibrium swelling of latex particles in the presence of the free monomer is regarded[31] as analogous to the equilibrium in the swelling of a cross-linked polymer in a solvent,

but in the present case the swelling is limited not by intermolecular bonds but by the interfacial energy between particle and aqueous phase. Such a treatment will yield the equation

$$2\Phi_m\sigma/RTr = -[\ln(1-\Phi_p) + \left(1-\frac{1}{\bar{p}}\right)\Phi_p + \chi\Phi_p^2], \qquad (18)$$

similar in form to the well known Flory–Huggins relation[32], in which Φ_m and Φ_p are the volume fractions of monomer and polymer in the swollen particle, σ is the interfacial tension, R the gas constant, T the absolute temperature, χ the monomer–polymer interaction parameter, and $\bar{p}$ the number-average degree of polymerisation.

It follows from formula (18) that the view that the concentration of monomer in a polymer–monomer particle is constant is strictly not entirely accurate, since Φ_m depends on the particle radius and the interfacial tension, which change during polymerisation. Since, however, the increase in particle radius is balanced by that in the interfacial tension, such constancy can be used as a good approximation. Calculations based on Morton's equation show that the concentration varies very little with particle diameter over the range 500–1000 Å, while the emulsifier content of the particle is 2–5% of the mass of monomer[33,34].

Constancy of the monomer concentration in a polymer–monomer particle and its equilibrium character, the latter due to the ability of a polymer particle to swell in the monomer, are supported by a fair quantity of experimental results[35,36], which continue to appear. For example, after separation of drops of monomer and determination of yield of polymer the concentration of styrene in a polymer–monomer particle has been calculated[37] as 5–6 M, which corresponds to the equilibrium swelling of polystyrene in its own monomer[38]. A similar value has been obtained from kinetic data[12], by using the departure from linearity of curves representing the accumulation of polymer at the instant of disappearance of drops of the monomer and from the monomer–polymer ratio. It has been shown also[37] that establishment of the equilibrium concentration of styrene in a polymer–monomer particle is not limited by diffusion, since the rate of diffusion of the monomer into latex particles exceeds its rate of polymerisation by 100–200%, which is entirely consistent with the classical theory of emulsion polymerisation.

Table 2. Emulsion polymerisation of styrene in the presence of ethylbenzene[39]*.

Ethylbenzene, %	c, M	R_{pp}	$[\eta]$, dm^3 g^{-1}	$c^2/[\eta]^{-1}R_{pp}^{-1}$, mole^2 g h dm^{-9}
0	8.69	1.99	1.60	2.4
10	7.82	1.66	0.90	4.1
25	6.57	0.63	0 65	10.5
50	4.35	0.17	0.34	32.7

*Here c is the concentration of styrene in the oil phase, $[K_2S_2O_8] = 0.01\%$, the concentration of sodium dodecyl sulphate in the oil phase is 2 mass %, and the phase ratio of oil to water is 1 : 2.

However, recent papers have indicated that an equilibrium concentration is not established in a polymer–monomer particle even during the emulsion polymerisation of styrene. In particular, the rate of the latter process is lowered by the presence of aromatic solvents to a greater extent than would correspond to the decrease in the monomer concentration (Table 2)[39]. Since the solvent does not diminish the number of particles (on the contrary, the number is slightly increased), it is concluded[39] that the diminished rate is due rather to a lower rate of polymerisation per particle R_{pp}. The latter decrease is attributed to a diminished viscosity in the latex particle and a consequent smaller contribution by the Trommsdorff effect, which may be evidenced by the considerable drop in intrinsic viscosity $[\eta]$ of the resulting polymer with increasing concentration of ethylbenzene. The viscosity decrease cannot be attributed solely to chain transfer to the solvent, since in this respect ethylbenzene is analogous to styrene itself. Calculation of $c^2/[\eta]R_{pp}$, associated with the ratio $k_{gr}/k_t^{1/2}$, shows that its variation at different ethylbenzene concentrations can be due only to change in the bimolecular termination constant if the rate constant of chain growth remains constant, which is quite probable.

Explaining the observed phenomena in terms of the Trommsdorff effect involves postulating firstly the existence of more than one radical in a polymer–monomer particle, which we have seen to be quite possible for sufficiently large particles, and secondly variation in the viscosity in the particle with solvent concentration. If ethylbenzene and styrene are assumed to be almost identical in thermodynamic properties, changes in viscosity should not have occurred in the particle, since the ratio of monomer plus solvent to the polymer, governed by the equilibrium between the oily phase in the drops and in the particle, would have been constant independently of the presence or the concentration of the solvent. However, the opposite is indicated by the fall in viscosity in the particle with increase in solvent concentration, deduced[39] from the diminution in the gel effect: i.e. replacement of part of the monomer by solvent leads to a ratio of monomer plus solvent to polymer which exceeds that of monomer to polymer when emulsion polymerisation occurs in the absence of a solvent. This result is regarded[39] as indicating non-equilibrium swelling of the polymer–monomer particle, the non-equilibrium character strengthening on passing to the system containing styrene alone (in absence of a solvent).

Other results[40] may also indicate that the swelling of polymer–monomer particles is not an equilibrium process. Halting it by cooling to and maintaining at 10 °C a system comprising styrene with azoisobutyronitrile and Ts-40 (oxyethylated hexadecanol $C_{16}H_{33}O.[C_2H_4O]_{40}H$) results in a higher rate of emulsion polymerisation after the system has been heated to 60 °C than in the normal method of polymerisation. It is supposed[40] that holding the system at 10 °C enables the particles to achieve equilibrium swelling, whereas under the usual conditions the concentration of monomer in a polymer–monomer particle is lower than the equilibrium value. In the Reviewers' opinion, however, these results[40] can have a different interpretation: in particular, the increase in rate after the reaction has been halted can be explained not by an increase in the concentration of monomer in the particle but by a change in the dispersity, e.g. as a result of quasi-spontaneous emulsification. Such experiments would undoubtedly have been more convincing if the reaction had been halted not at the micellar but at the steady stage, when particle formation is complete.

The above results[39,40] were obtained under fairly specific conditions, and can hardly be extended to the majority of traditional emulsion systems. The postulated[39] identity in the thermodynamic properties of the systems formed by polystyrene with styrene and with ethylbenzene appears to the Reviewers not entirely correct, since the parameter χ_1

representing polymer–solvent interaction may differ significantly for these systems. Values of χ_1 for the polystyrene–ethylbenzene system have not been published. Comparison of such systems as those of polystyrene with styrene, toluene, and xylene (with χ_1 respectively 0.33, 0.428, and 0.41)[41] shows that differences in thermodynamic properties between solutions of polystyrene in ethylbenzene and in styrene may be considerable. The above doubts concerning results in Ref.40 are supplemented by the use of a non-ionogenic emulsifier at fairly high concentrations, when formation of a stable structural layer may offer a mechanical barrier to penetration of the monomer into the proton–monomer particle. Nevertheless, as shown above, results obtained for systems with an ionogenic emulsifier at moderate concentrations usually indicate equilibrium swelling of such a particle.

VI. CONCENTRATION GRADIENT OF MONOMER

It is worth paying attention not only to the concentration but also to the distribution of the monomer in a latex particle, a problem hardly discussed at all until recently and arising from the investigations of Williams et al.[29,42–47] The essence of this worker's views is that the monomer is distributed non-uniformly in a polymer–monomer particle: a shell enriched in the monomer surrounds a core in which the polymer is concentrated. Since Williams' conclusions are fundamental in character, we shall consider his results in detail, taking into account the experimental conditions.

Table 3. Dependence of induction period in the emulsion polymerisation of styrene on time of polymerisation by concentration of inhibitor[29]*.

t, min	v, % h^{-1}	Inhibitor, g	τ, min
15	12.0	0.032	32.0
60	14.2	0.008	7.0
60	13.4	0.016	13.0
60	10.6	0.032	36.0
60	10.3	0.032	36.0
120	12.8	0.032	36.0
180	15.4	0.032	36.0

*Here t is the time of polymerisation, v the rate, and τ the induction period.

The "core–shell" theory of the polymer–monomer particle appeared as a consequence of kinetic data for the emulsion polymerisation of styrene on potassium persulphate in the presence of a mixture of sodium dodecyl sulphate and Triton X-100 (octylphenoxypolyethyleneoxyethanol)[42]. Grancio and Williams pointed out that stage (II), i.e. that before disappearance of drops of monomer, terminated at 30% conversion of styrene, whereas the rate of polymerisation remained constant until 50–60% conversion. Thus the concentration of monomer in a particle was roughly halved (from 6.3 M to 3.6 M) along the steady-state segment from 30% to 60% conversion. The number of particles and the number of radicals in them remained unchanged in the steady stage. Invariability of n was regarded[42] as indicated by the absence of an increase in the rate of emulsion polymerisation on introduction of an additional portion of initiator to the system in the steady stage.

Grancio and Williams[29] demonstrated the constancy of the rate of initiation by adding an inhibitor during the polymerisation of styrene (100 g styrene + 0.15 g sodium dodecyl sulphate + 3.0 g Triton X-100 + 0.075 g potassium hydroxide + 180 g water), when the induction period was directly proportional to the inhibitor concentration (Table 3). They adduced the interesting fact that the molecular weight of the polymer increases during the steady stage (Fig.6), contrary to traditional views. They give no clear explanation of the phenomenon, and attribute it to peculiarities of polymerisation in a polymer–monomer particle in the presence of a concentration gradient of the monomer.

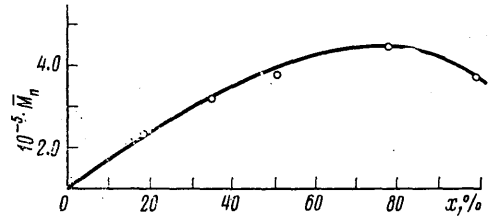


Figure 6. Variation of number-average molecular weight of polystyrene with conversion[29].

Williams explains the kinetic results by constant concentration conditions in the reaction zone, i.e. in the shell, in spite of variation in the monomer concentration calculated on the whole volume of the particle.

Kinetic data were accompanied by direct evidence of the formation of particles having a "core–shell" morphology[46]. Emulsion copolymerisation of styrene and butadiene on a polystyrene latex seed, with equilibrium saturation of the polystyrene particles by monomers added in the second stage, yielded particles comprising a polystyrene core and a shell formed from the added monomers. The structure of the particles was observed on electron micrographs of sections treated with osmium tetroxide.

Since this result appeared inconsistent with the simple thermodynamic incompatibility of polybutadiene and polystyrene, the inoculated polymerisation of styrene was undertaken[46] with a tritium-labelled polystyrene latex as seed, particles of which were saturated with styrene as before. Tritium gives β-rays of moderate penetrating power, which should be completely absorbed by a polystyrene shell 500–800 Å thick. An inoculating latex was therefore obtained having radioactive particles (diameter 1520 Å), on which non-radioactive styrene was polymerised to give a shell 1330 Å thick. The resulting particles were devoid of β-activity, from which it followed that the styrene had polymerised on the surface of the seed particles.

Williams suggested a theoretical explanation of the "core–shell" model on the assumption that the most probable, uniform distribution of polymer throughout the particle is prevented by its thermodynamic properties[45]. The latex particle is a microsystem, to which the laws of macrothermodynamics may be inapplicable. Indeed, only at the centre of a homogeneous particle can a macromolecule adopt the most probable conformation, i.e. one of high entropy. Macromolecules at the periphery, in a zone close to the interface, have diminished conformational entropy. In the "core–shell" model a macromolecule in the shell, which is a dilute

solution of the polymer, is able to adopt the most probable conformation.

The Williams theory has been seriously criticised by several well known investigators. Ugelstad[30] and Friis[27] doubted whether the kinetic data were correct, and considered that Grancio and Williams' results[29] could be explained in terms of the generally accepted increase in the number of radicals in a particle with increasing degree of conversion. Such a suggestion is quite plausible, since latex particles in the work of the Williams group were quite large ($d > 1000$ Å). In experiments with addition of initiator during polymerisation an increase in rate might have been overlooked, for it would have been only 7% under the conditions adopted.

Morton et al.[48] checked the data on the variation in molecular weight of the polymer with conversion and found that they involved experimental errors due to use of an impure specimen of the non-ionogenic surface-active agent—Triton X-100—which tended to oxidise rapidly in the air. The resulting functional groups of peroxy-type acted[48] as chain carriers, and the increase in molecular mass of the polymer could be attributed to their depletion during polymerisation. If Triton X-100 was replaced by an anion-active emulsifier (sodium oleate) or a mixture of dodecyl sulphate and the non-ionogenic surface-active agent Emulphogene BC-840 (tridecyloxypolyethylenoxyethanol), which is resistant to oxidation, no increase in molecular weight of the polymer is observed during the emulsion polymerisation of styrene.

Napper[49] accepts the existence of "core–shell" particles, but attributes formation of such a structure not to a thermodynamically improbable concentration gradient of the monomer across the particle but to specific aspects of the initiation of emulsion polymerisation by persulphates. Breakdown of a persulphate involves formation of radical-anions $SO_4^{\cdot-}$, which when initiating polymerisation fix one end of the polymer chain on the surface of the latex particle as a consequence of the strongly polar properties of the terminal sulpho-group. In inoculated polymerisation the growing macroradical attached to the surface "evacuates" monomer from the core, thereby being polymerised in the shell.

In reply to the critical comments Williams showed that the "core–shell" morphology is realised even in the initiation of emulsion polymerisation by benzoyl peroxide[46], although the thickness of the shell is substantially less than in the presence of potassium persulphate (respectively 155 and 520 Å) with inoculated polymerisation under similar conditions. In the latter case the size is almost equal to the diameter of the seed.

Gardon[50] also sharply criticised the "core–shell" theory. He considers that there are no thermodynamic grounds for expecting a concentration gradient of the monomer across the latex particle, as the coefficient of diffusion in the swollen polystyrene–styrene system should be $\sim 10^{-9}$–10^{-7} $cm^2\ s^{-1}$, so that polymerisation in the particle will be slower than diffusion. Gardon puts forward several hypotheses to explain the morphology of the particles observed by Williams: (i) the "core–shell" morphology in the system comprising inoculating polystyrene particles with styrene and butadiene is due to the incompatibility of polybutadiene and polystyrene; (ii) with tritium-labelled inoculating polystyrene particles and ordinary styrene the formation of inactive polystyrene in the shell may be expected to be due to reactions of chain transfer to the non-ionogenic emulsifier, a hypothesis supported experimentally, as shown above, by the work of Morton et al.[48]

The "core–shell" theory of particle morphology does not solve the problem of the concentration of monomer in a polymer–monomer particle. If drops of monomer disappear at 30% conversion of styrene, the monomer concentration in the particle should exceed 6 M (at 60 °C), appreciably larger than the equilibrium monomer concentration (~5 M). The reason for the complete transfer of monomer from drops to the particle at such low conversions remains completely incomprehensible, since this process is thermodynamically improbable because of the equalisation, at the instant of establishment of the equilibrium concentration in the polymer–monomer particle, of the chemical potentials of the monomer in the different phases.

Thus kinetic evidence for the "core–shell" morphology is clearly inadequate, and thermodynamic aspects also present several unresolved problems. However, there is no doubt that particles of complicated structure are formed in seeded polymerisation. The particle morphology observed by Williams may be supposed to be due, not to establishment of an improbable concentration gradient of the monomer in the particle, but to the specific conditions under which emulsion polymerisation takes place.

Although the "core–shell" theory involved several incorrect assumptions, a new line of research on emulsion polymerisation—the preparation of polymer dispersions containing particles of complicated structure—was stimulated by the work of Williams and his collaborators. It cannot be asserted that no such investigations had been made previously[51–55], but they have only recently[56–59] become at all purposeful, covering several applied fields of polymer chemistry (production of shock-resistant copolymers, novel types of rubbers, paints and varnishes). Latex particles of layered morphology enable materials of quite diverse properties to be obtained from a given pair of monomers. For example, dispersions of particles having hard cores and rubberlike shells can be regarded as a source of reinforced elastomers. Rubberlike particles having a thin solid-polymer shell give readily processable non-stick rubbers. Particles with a rubber core and a solid-polymer shell provide a typical system for the preparation of shock-resistant copolymers. Application of a thin layer of a soft polymer to a hard core is able to confer good film-forming properties on a dispersion.

Three methods are in practice available for obtaining latex particles of layered morphology in the course of inoculated polymerisation—(i) exploitation of incompatibility between seed polymer and polymer formed in the second stage, (ii) use of monomers that are pore solvents for the seed polymer, and (iii) conducting the second stage of polymerisation under conditions such that the seed particles are unable to swell in the added monomer, i.e. under conditions of competition between rates of diffusion and of polymerisation.

As examples of these procedures we may mention (i) the preparation of shock-resistant ABS copolymers by the emulsion method, (ii) the polymerisation of vinyl chloride or vinylidene chloride, and (iii) the polymerisation and copolymerisation of acrylic monomers. The last process has been developed especially successfully by Eliseeva et al.[58] However, these investigations lie outside the scope of the present Review. We note merely that realisation of the "core–shell" particle model has enabled film-forming dispersions to be obtained with properties considerably surpassing those of dispersions obtained by the random copolymerisation of acrylic monomers or by mixing two acrylic lattices[59].

VII. PRIMARY REACTIONS OF POLYMERISATION IN EMULSION SYSTEMS

The way in which primary actions occur during emulsion polymerisation differs substantially from that observed for homogeneous systems, as is apparent in the values of the constants and in the molecular characteristics of the resulting

polymers. One of the chief distinctions between emulsion and homogeneous systems lies in the possibility of segregating primary reactions in separate phases. This explains the unique feature of emulsion systems that the rate of polymerisation and the molecular weight of the resulting polymer both increase with the concentration of the emulsifier.

Since increase in emulsifier concentration entails an increase in the number of latex particles, the rate of emulsion polymerisation increases. With a constant rate of formation of free radicals in the aqueous phase the increased number of particles leads in turn to a diminished probability of entry of a radical into any polymer–monomer particle: i.e. the lifetime of a radical growing in a particle lengthens, so that the molecular weight of the polymer increases with the emulsifier concentration. We can use this feature of emulsion systems to obtain polymers differing fundamentally in properties from those obtained in homogeneous systems.

1. Initiation

As we have already seen, the number of particles in an emulsion system—one of the chief kinetic parameters—is determined in considerable measure by the rate of initiation. After the stage of formation of polymer–monomer particles is complete, the rate of the process no longer depends on the rate of formation of radicals. Thus introduction of a fresh portion of initiator in the steady stage produces no change in the rate of polymerisation. After completion of particle formation the rate of initiation affects only the frequency of acts of interconversion of particles between "dead" and active states, i.e. the molecular mass of the polymer. All these considerations apply, of course, to cases in which a particle can contain at most one radical.

The initiation of emulsion polymerisation is studied mainly on water-soluble inorganic peroxo-compounds such as ammonium and potassium persulphates, with which initiation is highly efficient (close to unity)[60]. Although many papers have appeared on the kinetics and the mechanism of the breakdown of persulphates in aqueous solution[60–64], the influence of emulsifiers on the rate has remained obscure[65–67]. In the majority of systems the presence of an emulsifier slightly accelerates the decomposition of persulphates. The considerable increase in rate in aqueous media at low pH is due to a change in the reaction mechanism[68,69].

The influence of aqueous solutions of surface-active agents on the kinetics of the decomposition of organic peroxy-compounds, e.g. hydroperoxides, is a more complicated problem. Here the increase in rate of decomposition may be due to several causes. On the one hand, the presence of an aqueous medium leads to the breakdown of association complexes of hydroperoxides, which differ in thermal stability from the monomeric hydroperoxides[70]. On the other hand, the accelerating action of the surface-active agent may be explained by the effects of micellar catalysis[71], which develops during the concentration of bifilar hydroperoxide molecules in emulsifier micelles. The action of an adsorbed film of polymer–monomer particles is probably similar, exerting a concentrating and orientating influence on hydroperoxide molecules and leaving such relatively non-polar initiators as benzoyl peroxide unaffected[72].

Artificial attachment of an initiator in the region of an adsorbed layer of polymer–monomer particles produces, independently of its polarity, a marked change in its rate of decomposition and hence in the rate of initiation of polymerisation. Thus the Reviewers have shown[114] that the graft polymerisation of styrene on particles of an inoculating latex—a copolymer of n-butyl acrylate and 1-t-butylperoxyethyl methacrylate—takes place at considerably higher rates in the emulsion than in the bulk or in a solvent at lower temperatures. It is sufficient to note the mere fact of polymerisation at a high rate under the influence of a dialkyl type of peroxide at an abnormally low temperature (in the bulk hardly any polymerisation occurs under corresponding conditions).

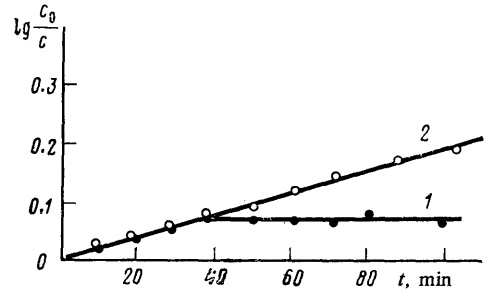


Figure 7. Semi-logarithmic transforms of kinetic curves for the decomposition of peroxy-groups in a copolymer of n-butyl acrylate and 1-t-butylperoxyethyl methacrylate (6.5 mole % of permonomer units in copolymer) in a latex of mean particle diameter 0.100 μm at 60 °C for different distributions of peroxy-groups in latex particles: 1) uniform; 2) predominantly in surface zone[73].

The decisive influence of an adsorbed film on the kinetics of initiator decomposition is also indicated by the difference in the kinetics of the breakdown of peroxy-groups in the copolymer according to their distribution through the latex particle (Fig.7)[73]. The results confirm that under selected conditions breakdown occurs predominantly at the particle surface. With a uniform distribution of peroxy-groups through the particle only the small proportion located at the surface decompose. The surface distribution of peroxy-groups achievable by proportioning the monomers in the preparation of the latex ensures that they will be almost completely decomposed.

Emulsion systems are very convenient for the use of redox initiating systems, in which phase separation of components is possible, so that radical formation can be localised at the interface. Interesting effects are obtained by the use of specifically acting emulsifiers capable of influencing the mechanism of the breakdown of peroxide initiators. Cation-active emulsifiers containing a quaternary nitrogen atom have been investigated in the greatest detail[74–78]. The activating effect of such surface-active agents on the initiation of emulsion polymerisation is attributed by most authors to conversion of the quaternary compounds into tertiary amines[21], whose accelerating action on the decomposition of peroxy-compounds is well known. Such effects were discovered on cationic surface-active agents such as alkylpyridinium halides[74–76]. The unexpectedly high rates of polymerisation in the presence of surface-active aliphatic quaternary ammonium salts were attributed to the formation of tertiary amines[22,77,79] by the Hofmann decomposition of the quaternary compounds. Direct involvement of such compounds in acts of initiation is indicated by the antiparallel dependence, unusual for emulsion polymerisation, of the rate of polymerisation of styrene and the molecular weight of the resulting polymer on the emulsifier concentration (Fig.8)[22].

We can thus consider two specific aspects of the initiation of emulsion polymerisation. Firstly an indirect influence on the overall kinetics can be expressed as the dependence of the number of polymer–monomer particles in the emulsion system on the rate of initiation, which ultimately determines the kinetics of the process. On the other hand, the rate of decomposition of the initiator, and hence the rate of radical formation, depend on the properties of the emulsion system itself, the distribution of initiator between aqueous and oil phases, the possibility of localising acts of initiation in the region of adsorbed layers of emulsifier, and in individual cases direct chemical action of the initiator on the actual acts of radical formation.

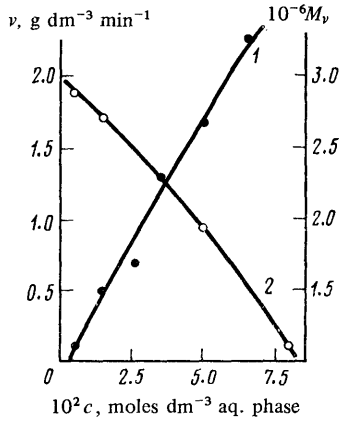


Figure 8. Effect of concentration c of emulsifier (Alkamon DS), with cumene hydroperoxide (0.01 mole cm^{-3} styrene) as initiator and phase ratio of monomer to water 1 : 7, on: 1) rate of polymerisation of styrene: 2) molecular weight of polymer[22].

Since in this work polymerisation was conducted at low temperatures, because of the presence of a redox initiating system, the reliability of these views is doubtful. According to Dunn[82] the low temperatures themselves can explain some regulating effect in the chain-growth steps, for isotactic and syndiotactic additions differ in activation energy[83]. The fact that the ratio $k_{gr}/k_t^{1/2}$ remained unchanged (Fig.9) when styrene was polymerised in the presence of Alkamons—cationic surface-active agents[12]—in media of differing pH, when the state of the adsorbed layer of emulsifier and the rate of initiation of polymerisation varied greatly owing to passage of nitrogen into the amine state, indicates that the adsorbed emulsifier film had no effect on acts of chain growth.

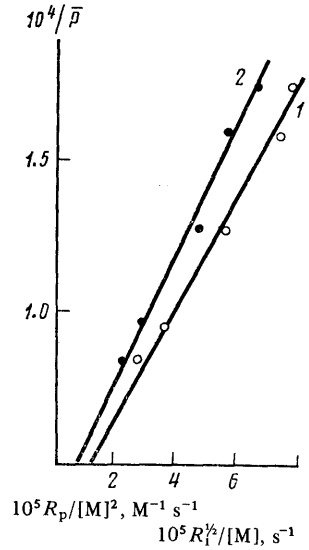


Figure 9. Dependence of reciprocal of polymerisation on $R_p/[M]^2$ and $R_i^{1/2}/[M]$, where the concentration of the monomer in the polymer–monomer particle [M] = 5 M.[12]*

2. Chain Growth

It is usually supposed that chain growth during polymerisation in an emulsion proceeds as in homogeneous systems, i.e. with the same kinetic constants. This postulate enables the chain-growth rate constant to be calculated by means of Eqn.(5) for the rate of emulsion polymerisation. In many cases the results agree well with values of k_{gr} calculated in other ways[34,38,80].

Nevertheless, the view has been expressed that an adsorbed layer of emulsifier has a direct effect on the primary acts of chain growth[21,81]. Such ideas are based mainly on studies of emulsion polymerisation in the presence of *N*-alkylpyridinium halides as cation-active emulsifiers. Thus Medvedev assumed[21] that conducting emulsion polymerisation in an alkaline medium favours conversion of quaternary nitrogen into the amine state with appearance of an initiating centre on the emulsifier molecule. A regular arrangement of charged and uncharged nitrogen atoms on the surface of a latex particle is regarded as ensuring stereocontrol of chain growth and yielding polymers of more regular structure than in the usual cases of emulsion polymerisation.

Specific emulsion systems exist in which such an effect has been quite definitely established. The emulsion copolymerisation of styrene with maleic anhydride in the presence of lecithin as optically active surface-active agent yields an optically active copolymer[84]. However, this result can be explained by separation of the two comonomers in different phases as a consequence of differences in aqueous and mutual solubility. Since maleic anhydride is incapable of homopolymerisation under ordinary conditions, it does not polymerise in the aqueous phase, despite initiation by a water-soluble initiator such as potassium persulphate. Thus copolymerisation can take place only at the interface, i.e.in the region of adsorbed layers of surface-active agent. As a result lecithin exerts a direct influence on chain growth.

Thus the above examples show that under certain conditions surface-active agents can affect acts of chain growth, although in most trivial emulsion systems such an influence is improbable if not impossible.

*It seems that the wrong diagram may have been taken from Ref.12 (Ed. of Translation).

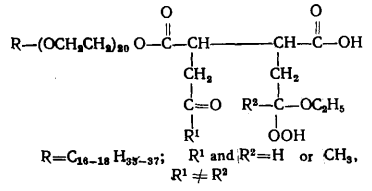
3. Chain Termination

Clearly, it makes sense to speak of bimolecular termination of two growing macroradicals during emulsion polymerisation only when two or more radicals can in principle be present in the polymer–monomer particle. As already noted, this case occurs with sufficiently large particles (of diameter ~1000–1200 Å), in which the primary radical grows to a certain size "without terminating" an already existing macroradical in the given particle, and is able to lose mobility owing to its increase in size and the high viscosity of the particle. Several workers have shown[12,85] that in such cases the termination rate constant k_t has the extremely low values characteristic of polymerisation in highly viscous media. Furthermore, although this constant remains almost unchanged at the steady stage with a constant concentration ratio of monomer and polymer in the particle, it decreases after drops of the monomer have disappeared, owing to enhanced viscosity in the particle, which in turn causes an increase in the number of radicals in the latter[27].

When only one radical can be present in a particle, chain termination by the first radical to enter the particle takes place instantaneously. As a consequence the molecular weight of the polymer is determined solely by the frequency of entry of radicals into a particle, i.e. by the rate of initiation. Since with a high degree of dispersion of the emulsion system this frequency is not too high, the lifetime of a free radical is considerably longer in emulsion polymerisation than when polymerisation occurs in the bulk or in solution. As a result, polymers of quite high molecular weight are obtained by emulsion polymerisation.

Especially interesting effects arise when the generation of free radicals is suddenly arrested (with light or radiation as initiator). In this way the lifetime of a radical present in a polymer–monomer particle may become indefinite, and the use of postpolymerisation effects will yield polymers of exceptionally high molecular weight, provided that chain transfer to monomer, emulsifier, or impurity is not too intense. Polystyrene of molecular weight $>10^7$ can be obtained[25,86] by emulsion postpolymerisation. The latter effects can be used also to obtain graft and block copolymers[25,86–88].

It was supposed until recently that these phenomena—formation of polymers of abnormally high molecular weight and also block copolymers—are possible only with the emulsion system exposed to light or radiation. However, it has now been shown[89–95] that such effects can be obtained also with peroxide initiation of emulsion polymerisation. Quite a high rate of polymerisation is observed in the emulsion polymerisation of methyl methacrylate in the absence of specially introduced initiator[89], i.e. under the influence of peroxides formed by oxidation of the emulsifier, and the molecular mass reaches 7×10^6. Still higher molecular masses (up to 2×10^7) can be obtained by using the initiator



specially synthesised by the Reviewers[114], which possesses well defined surface-active properties.

The emulsion polymerisation of styrene goes at normal rates when the concentration of this initiator is 10^{-6}–10^{-7} M in the monomer. This phenomenon cannot be attributed to a high efficiency of initiation, since separate experiments showed that the efficiency did not exceed a few percent. The reason must be sought in a lengthened lifetime of the radical in the polymer–monomer particle, ensuring the formation of polystyrene of exceptionally high molecular mass (up to 2×10^7). It is as yet difficult to explain satisfactorily the effects arising when acts of initiation are localised in an adsorbed layer of emulsifier. It may be supposed that they are related to additional restriction of the mobility of the growing radical by the attachment of one end to the particle surface, with a consequent decrease in the termination constant. It is noteworthy also that the use of such emulsifying initiators at normal concentrations (0.01 M in the monomer), because of chemical bonding with the resulting polymer, produces polymer dispersions of enhanced resistance to electrolytes, mechanical distortion, and freezing[96].

Very interesting phenomena have been observed by the use of polymeric initiators. Mikulašova et al.[91–94] have investigated the emulsion polymerisation of styrene in the presence of a polymeric hydroperoxide obtained by the oxidation of polypropylene. The hydroperoxide was used as a powder of particle size 0.1–0.55 mm in the presence of triethylenetetramine combined with metals of variable valency to activate breakdown of the hydroperoxide. Styrene was polymerised at 20–50 °C with ionogenic (sodium alkanesulphonates) or non-ionogenic surface-active agents as emulsifier. A feature of this polymerisation system is that the molecular mass of the polymer increases with time. For example, it approximately doubled when the degree of conversion of styrene changed from 4% to 12%. When the polymeric hydroperoxide was replaced by a mixture of polypropylene and t-butyl hydroperoxide, the molecular weight of the polymer did not change with conversion and its value was some 10% of that in the system containing the polymeric hydroperoxide. Use of a polymeric initiator will yield polystyrene of exceptionally high molecular mass (2×10^7) with a very narrow molecular-mass distribution ($M_w/M_n = 1.01$). Similar results have been obtained by the same workers[95] by using oxidised powdered graphite or silica to initiate the emulsion polymerisation of methyl methacrylate.

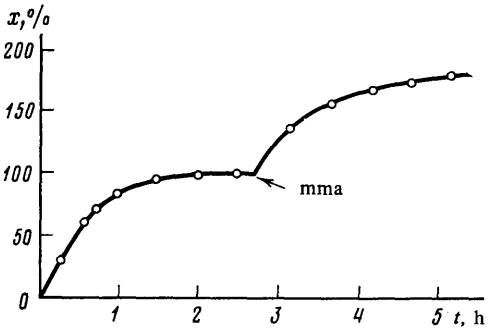


Figure 10. Kinetic curves for the polymerisation of styrene and that of methyl methacrylate (mma) on "live" polystyrene during emulsion polymerisation initiated by polypropylene hydroperoxide[90].

Another feature is the possibility of obtaining block copolymers[90]. Introduction of a second monomer following complete depletion of styrene led to a resumption of polymerisation

(Fig. 10). Formation of block copolymers has been proved by turbidimetric titration[90].

The above facts are regarded[90-94] as evidence of polymerisation without termination of growing radicals, i.e. by a mechanism of live chains. In the first stage of a suggested two-stage mechanism chain growth takes place on the surface of polypropylene, when under certain conditions grafts of polystyrene do not take because of the special mechanism of initiation by polypropylene hydroperoxide and triethylenetetramine[91]. As the molecular weight of polystyrene increases, it becomes more incompatible with polypropylene. As a result the macroradical becomes detached from the polypropylene surface and passes into the aqueous phase, to form on absorption of a monomer and stabilisation by the emulsifier a polymer–monomer particle. In the second stage the process continues in the particles by a "non-terminable" mechanism, since primary radicals from the aqueous phase do not penetrate the particle, and their formation within the particle is also excluded.

The suggested mechanism explains the results, but cannot yet be accepted without question. Other workers[97,98] have used methods similar to those of Mikulašova et al. to obtain block copolymers of vinyl chloride, but have interpreted their results on a different basis. Two types of radical-forming groups—hydroperoxy and peroxy—are present in oxidised polypropylene[97,98]. The former, which are less thermostable, initiate the emulsion polymerisation of styrene or acrylic esters in the first stage at 30–40 °C. In the second stage, after introduction of the second monomer, the process continues at 50 °C on the more thermostable peroxy-groups, whose presence in the polymer isolated after the first stage was demonstrated in separate experiments. It was also shown that such a polymer is able to initiate polymerisation not only in an emulsion system but also in the bulk, although the latter requires a higher temperature (70 °C).

In contrast to the concept of "live" radicals, the polyfunctional nature of the polymeric initiator is used[97,98] to explain the observed effects. However, the proposed mechanism is not entirely consistent with the molecular-weight characteristics of the resulting polymers. The narrow molecular-weight distribution and the M_w/M_n ratio close to unity, observed in the work of Mikulašova, are not achieved in polymers obtained on polyfunctional initiators with peroxy-groups varying in thermal stability[99], and are more typical of processes occurring on long-lived active centres without chain termination.

We note in conclusion that chain-terminating reactions are considerably slower in emulsion systems than in homogeneous polymerisation, owing to the low termination rate constants and the isolation of growing radicals in individual particles. These circumstances ensure the formation in emulsion polymerisation of polymers having exceptionally high molecular masses, and in limiting cases the occurrence of polymerisation without chain termination.

VIII. TOPOCHEMISTRY

We shall now consider the sites at which latex particles are generated and the mechanism of their formation. We have already discussed this problem in terms of the views of Harkins[7,8] and of Yurzhenko[9,10] on the appearance of particles in emulsifier micelles, a quantitative basis for which was given by Smith and Ewart. However, micellar nucleation of particles under the influence of primary radicals is by no means the only possible mechanism, is unable to **explain** several features of emulsion polymerisation, and **is quite** inapplicable to certain specific systems, e.g. emulsion polymerisation in the absence of an emulsifier. The problem of the nature of the primary radical entering the micelle was ignored in the early work. Nevertheless, the need to pose this question is evident in the initiation of emulsion polymerisation by persulphates, which generate active centres of radical-anion type. It is difficult to imagine that the highly polar charged species SO_4^- is capable of penetrating a similarly charged micelle (anionic surface-active agents have been used in almost all studies of the topochemistry of emulsion polymerisation).

These difficulties led to the view that emulsion polymerisation was initiated directly in the aqueous phase, oligomeric radicals were formed and penetrated into micelles (because they were sufficiently hydrophobic) or were precipitated into the aqueous phase on reaching a critical molecular mass, and nucleation took place by a non-micellar mechanism[100-102]. The fundamental ideas of the theory of homogeneous nucleation were developed by Fitch[101,102] and based on the postulate that radicals were formed in the aqueous phase and captured by already formed particles at the same rate. He proposed an equation in which the rate of capture of radicals ρ_c was proportional to the total particle surface. The theory was used to describe the polymerisation of methyl methacrylate in very dilute aqueous solution. In the absence of an emulsifier the primary particles are stabilised by ions formed on decomposition of the initiator. According to the theory of the homogeneous nucleation of particles the addition of an emulsifier does not increase the number of particles formed but merely tends to enhance the stability of the primary particles and prevent their flocculation. The theory was developed primarily for polar monomers readily soluble in water, but was later applied also to such sparingly soluble monomers as styrene.

Roe suggested[103] that particles are formed also outside micelles in the emulsion polymerisation of styrene, and their formation ceases at the instant when the total particle surface reaches a value at which the emulsifier concentration in the aqueous phase becomes lower than the critical concentration of micelle formation. He showed that this hypothesis leads to the same formula for the number of particles as does the Smith–Ewart theory.

Peppard showed[104] that the Fitch theory is fully applicable to the emulsion polymerisation of styrene at low emulsifier concentrations. At higher concentrations nucleation takes place both in the aqueous phase and in micelles. This theory assigns great importance to the rate of capture of oligomeric radicals by particles. In deducing the equation for this rate Fitch used collision theory, and assumed that every collision between a radical and a particle leads to capture. The rate of capture of radicals is then given by the equation

$$\rho_c = \pi r^2 L w_i N,$$

where L is the mean distance a radical diffuses in the aqueous phase before it grows to a size at which it separates from this phase as a primary particle.

Barrett has shown[105] that the Fitch formula presupposes movement of the oligomeric radical along a straight line, so that the probability of its collision with a primary particle is greatly underestimated. The rate of capture of radicals can be calculated from diffusion theory on the assumption that their adsorption is reversible, by means of the equation

$$\rho_c = 4\pi r D_j N R_j,$$

in which D_j is the coefficient of diffusion of long-chain radicals in the aqueous phase and R_j their concentration in this **phase.** This formula indicates a higher rate of capture of **radicals than** that calculated by means of the Fitch expression.

The theory of homogeneous nucleation has now been fairly well developed, but no direct experimental evidence of the existence of surface-active radicals has yet been found. One of the most convincing indications of their formation in the aqueous phase is the decrease in surface tension during the initial stages of emulsion polymerisation[106]. A recent investigation[107] of the polymerisation of styrene in aqueous medium in the presence of potassium persulphate (with an alkanesulphonate as emulsifier) at a low monomer concentration has given results that can be regarded as kinetic proof of the homogeneous nucleation of particles. In the initial stage the rate of polymerisation corresponds to an order of reaction 0.5 with respect to the initiator. The molecular mass of the resulting polymer is proportional to the initiator concentration to the power −0.5 up to 20% conversion. These results indicate bimolecular termination of growing chains, which is characteristic of steady-state kinetics of radical polymerisation in a homogeneous system. Hence it may be concluded that in the initial stage polymerisation takes place under homogeneous conditions, i.e. in the aqueous phase. In later stages the process moves from the aqueous phase into the resulting polymer–monomer particles, as is evident in the kinetics: the rate of polymerisation increases owing to the higher monomer concentration in the particles than in the aqueous phase, while the order of reaction with respect to the initiator falls to 0.26 at 30% conversion.

Table 4. Variation of particle diameter and number in unit volume with conversion[20] (0.870 M styrene + 3.69 mM $K_2S_2O_8$ at 70 °C).

t, min	x, %	$\bar{d}$, Å	$10^{-12}N$, cm^{-3}
15	0.4	700	1.90
30	0.8	930	1.23
60	2.1	1500	1.02
112	5.8	2140	0.97
175	12.9	2820	0.95
232	21.6	3250	1.04
292	32.3	3770	1.00
342	47.6	4120	1.12
1440	90.6	5030	1.18

A mechanism of homogeneous nucleation is more evident in emulsion polymerisation without an emulsifier. Interesting results indicating the existence of oligomeric radicals and the formation of primary particles on their precipitation from the aqueous phase have been obtained by Wilkinson et al.[19,20,108,109], who measured particle diameter and molecular weight of the polymer from low monomer conversions in the emulsion polymerisation of styrene in the presence of potassium persulphate. Table 4 shows that N changes appreciably only in the earliest stages of polymerisation. The molecular mass changes abruptly also only at the start of polymerisation, formation of a polymer of molecular mass ~1000 being observed in the earliest stages[20]. This last fact can probably be regarded as direct evidence of the presence of oligomeric radicals in the polymer system.

Another interesting phenomenon observed by Wilkinson et al. is the abnormal particle structure revealed on electron micrographs, shown diagrammatically in section in Fig.11. Such particles were observed by means of a scanning electron microscope, and their formation was attributed to removal of monomer from the inner region of a particle during vacuum preparation of the specimen. Particles having this structure were observed when specimens of latex were withdrawn at comparatively low conversions (~40%). This structure is supported also by results for the sorption of nitrogen by polymer particles after removal of monomer from them[19]. The total particle surface calculated by the method of Ref.17 exceeds by 17% the surface calculated from electron-microscopic data on the assumption that the particles are spherical in form.

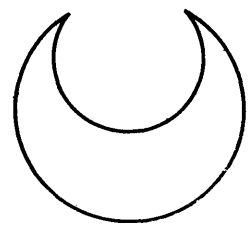


Figure 11. Structure of abnormal particle[17].

Wilkinson et al. explained the results in terms of a mechanism of the emulsion polymerisation of styrene in the absence of an emulsifier[20] involving formation in the early stages of a large number of primary particles of a polymer of low molecular weight. This is followed by flocculation of the primary particles to give stable particles, in which the usual emulsion polymerisation initiated by oligomeric radicals then proceeds. Thus the core of a particle is enriched with a polymer of low molecular weight. Since the solubility of the monomer in this polymer is higher, the inner region of the particle has a higher monomer concentration than has the outer region: i.e. a concentration gradient of the monomer is established in the polymer–monomer particle, although the concentrations themselves have equilibrium values in corresponding regions of the particle.

In a novel topochemical picture of emulsion polymerisation—the formation of polymer–monomer particles without involving emulsifier micelles—the particles are generated not in micelles but directly from drops of monomer[40] by quasi-spontaneous emulsification in conformity with the views of Taubman et al.[110] Transfer of monomer from drops to particles then takes place not by diffusion through the aqueous phase but as a result of direct contact, when obviously particle–particle contact is also possible.

Support for these views was sought[40] by using a new technique to obtain electron micrographs of latices at low conversions. The latex was frozen above the freezing point of styrene, and then the monomer was completely polymerised by exposure to fast electrons. Three kinds of particles—small (150 Å) corresponding in size to solubilised micelles, medium (600–800 Å) corresponding to polymer–monomer particles, and large (5000 Å) to drops of the monomer—can be observed on the photomicrograph. The polymerisation of styrene was conducted in the presence of the ionogenic surface-active agent E-30 (sodium pentadecanesulphonate) (4 wt.%) and azoisobutyronitrile (0.15 millimole in 1 ml of styrene) at 60 °C. As emulsion polymerisation proceeded, the size of the large particles diminished, that of the medium particles increased, and the small particles remained

unchanged. On addition of fresh portions of surface-active agent at conversions of 15% and 40% new polymer–monomer particles were formed significantly larger than micelles but smaller than the previously formed particles, with a consequent bimodal particle-size distribution (Fig.12).

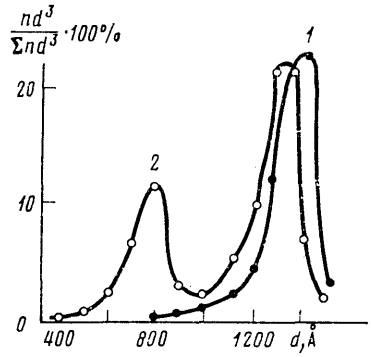


Figure 12. Size distribution of latex particles in presence of 0.15 millimole of azoisobutyronitrile in 1 cm^3 of styrene: 1) without additive; 2) after addition of Ts-40.[40]

However, these ideas are not consistent with such a well known fact as the abrupt increase in rate of emulsion polymerisation when the emulsifier concentration passes through the critical limit of micelle formation, which indicates that micelles play a definite part. Results of this type have been published recently by Smirnov et al.[111] Study of the traditional system comprising styrene with potassium peroxodisulphate and potassium laurate showed that in the region of this critical concentration a break occurs in the dependence both of rate of emulsion polymerisation and of number of particles on the concentration of surface-active agent. With regard to the results on additions of emulsifier during polymerisation, the comparatively large size of the newly formed particles can be explained by the greater rate of polymerisation in them consequent on the more developed surface and the higher probability of capture of monomer and free radicals.

The mechanism by which the small particles retain their size during polymerisation is not entirely clear. It may be supposed that the micellar stage of polymerisation was not yet complete [fairly high concentration (4%) of surface-active agent], but the phase ratio unfortunately was not given[40]. Furthermore, fine particles can be formed by the escape of radicals from polymer–monomer particles and nucleation by a homogeneous mechanism. Since homogeneous nucleation is possible at any stage of polymerisation, the apparent retention of size due to small particles may be caused by their continual regeneration during the process and flocculation with each other and with existing particles. Nucleation of particles in the aqueous phase has been used by Ugelstad et al.[112] to explain the formation of new particles finer than drops of the microemulsion obtained in the presence of the emulsifying system comprising a long-chain aliphatic alcohol with an ionogenic surface-active agent; the effect is observed whether the polymerisation of styrene in microdroplets is initiated by water-soluble or oil-soluble initiators.

Thus the results presented in Ref.40 undoubtedly indicate that microemulsification may make a certain contribution to the mechanism of the generation of polymer–monomer particles, but is not the sole cause and probably acts together with a micellar mechanism.

In a more recent study[113] on the same materials Pravednikov, Gritskova, et al. have developed the above ideas, while accepting the emphasis on the site at which polymerisation occurs in a polymer–monomer particle once formed. They worked with an oil-soluble initiator, and considered that effective polymerisation was possible only in cases in which the radicals formed were rapidly fixed in a polymer matrix, since under ordinary conditions the presence even of the two radicals produced by breakdown of a single initiator molecule cannot occur in a small polymer–monomer particle. However, the monomer content of such a particle is quite large, amounting to ~50% of its mass, and such a strongly swollen gel can hardly ensure effective fixation of radicals. This contradiction was explained on the hypothesis that the polymer separated out and formed a film at the particle–water interface. Thus a particle comprises a core strongly swollen in the monomer and a surface layer containing a small quantity of monomer, radicals being fixed in this layer.

Virtually the same arguments—bimodal molecular-mass distribution (with 10^{-6} M_n respectively 0.17 and 4.0) and formation of particles of abnormal structure—were used to support these hypotheses[113] as by Wilkinson[19,20], but with a different interpretation of the results. According to these workers[113] the polymer of low molecular weight is formed in the central region of the polymer–monomer particle as a result of rapid termination of unfixed radicals; the main site of polymerisation is the shell of the particle.

However, formation of a polymer of low molecular weight during emulsion polymerisation can be explained more simply by chain transfers to impurities that may be present in the reactants, phenomena that have been reported recently with styrene[48]. Furthermore, it is difficult to imagine the formation of a "low-molecular polymer" of molecular weight 170000 by the suggested[113] mechanism, since in a small particle termination would occur almost instantaneously with formation merely of oligomeric molecules. Since chain transfers take place predominantly in the early stages (their contribution should diminish as the carrier becomes exhausted), Wilkinson's explanation—greater solubility of the monomer in the core enriched with the lower polymer—can be accepted for the formation of abnormal particles.

Concluding our discussion of the mechanism of nucleation we note that local zones of particle generation in an emulsion system may vary depending on the specific conditions. In the absence of an emulsifier nucleation can occur only in the aqueous phase, i.e. by a homogeneous mechanism. In the presence of high emulsifier concentrations micelles form the chief site of nucleation. In the formation of microemulsions initiation of polymerisation and hence formation of polymer–monomer particles take place directly in microdrops. Even in the last two systems, however, it is probably impossible to eliminate the contribution of homogeneous nucleation.

For ordinary emulsion systems it is difficult to state unambiguously the site of polymerisation in an already formed particle (whether throughout or predominantly near the surface). However, the process can be localised predominantly in the outer zone of the particle by establishing special conditions (e.g. lower rate of diffusion of monomer into the particle). As a consequence it is entirely possible to realise a "core–shell" particle model, especially with inoculated emulsion polymerisation, when the polymer of the seed particles is thermodynamically incompatible with the polymer formed from the monomer introduced into the seed.

IX. CONCLUSION

The present Review cannot claim full coverage of published information on the theory of emulsion polymerisation that has appeared even during the past decade. The volume of information on such polymerisation increases steadily, the range of problems discussed widens, and at the same time investigators are returning to fundamental theoretical problems posed more than thirty years ago, attempting in individual cases to revise the basis of classical ideas. We have tried to examine only some of the most interesting lines of development of the theory of emulsion polymerisation.

Research on emulsion polymerisation during recent years has been characterised by experiments under special conditions enabling a specified topochemical and kinetic pattern to be modelled. Investigations in special model systems are extremely promising, since they enable individual parameters to be fixed that often are not entirely definite under ordinary conditions, and the sites at which primary processes occur to be established more precisely. Smith and Ewart's concept that the number of particles in an emulsion system is the principal kinetic factor in emulsion polymerisation remains most fruitful in current as in earlier work. Great attention is now paid to the structure of polymer–monomer particles and the site of polymerisation. The possibility under certain conditions of localising chain growth in particle shells indicates that particles of complicated structure may be formed.

The work surveyed thus shows that extremely diverse phenomena are observed during emulsion polymerisation, which cannot yet be explained in terms of a single theory. However, if we confine our attention to monomers that are sparingly soluble in water, the basis for a general theory probably does exist. The most practicable method is evidently still to seek general relations between conditions and the most important parameters (number of particles, local zone in which process occurs, primary constants). The classic Smith–Ewart theory, where such relations have been established, can be extended only to a limited number of systems. There is probably no need to revise this theory radically, as several authors attempt to do; it is advisable to define more clearly the limits of its applicability. Refinements and developments of certain of its principles are necessary and useful for obtaining more general ideas on emulsion polymerisation.

The work surveyed in this Review is not yet able to introduce full clarity into the theory of emulsion polymerisation, but is undoubtedly of both theoretical and practical interest, since it opens up new opportunities for the emulsion synthesis of polymers. In this connection we must again mention the work of Williams et al., which stimulated research on the preparation of polymer dispersions containing particles of layered structure, and the investigations of Mikulašova et al. on emulsion polymerisation in the presence of polymeric initiators, which enabled block copolymers to be obtained in emulsion systems. Research on emulsion polymerisation in the presence of multifunctional emulsifiers merits attention, in particular on surface-active initiators, which ensure the formation of polymers having exceptionally high molecular weights and latices that are highly resistant to various factors.

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Conjugated Inorganic Carbon-based Polymers

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Polymers of different types based on dicyanogen, dithiocyanogen, carbon suboxide, and carbon subsulphide, which exhibit conducting or semiconducting properties, are examined. The methods of synthesis, the polymerisation mechanisms, and the chemical and physical properties of these polymers are discussed.
The bibliography includes 192 references.

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I. INTRODUCTION

Wide interest has been manifested in recent years in the study of compounds with electronic properties and of a quasi-one-dimensional or quasi-two-dimensional character. Intense investigation of low-dimensional structures was stimulated by Little's familiar idea[1] of the possibility of creating high-temperature superconductors on their basis. Solids such as charge-transfer complexes (CTC) of the tetracyanoquinodimethane–tetrathiofulvalene type, mixed valence platinum complexes (KCP)† type, $K_2Pt(CN)_4Br_{0.30}\cdot.2.3H_2O$, etc., have since become classical examples of systems which exhibit a whole series of collective phenomena associated with their quasi-one-dimensionality[2]. These phenomena as well as the concepts developed to account for them can be transferred also to certain polymers. With the aid of chemical methods, it is possible to predict the existence of a whole class of materials with extremely remarkable electrical and magnetic properties[2]. Since 1973, polysulphonitride $(SN)_x$, which is the first example of polymers with a metallic conductivity ($\sim 10^3\ \Omega^{-1}\ cm^{-1}$ at room temperature), has been studied vigorously. Furthermore, near 0.3 K there is a transition to the superconducting state; this discovery demonstrated the possibility, in principle, of the existence of superconductivity in a system without metal atoms. Detailed investigations in recent years[3] have shown that $(SN)_x$ is not in fact a one-dimensional system; it would be more correct to regard it as a highly anisotropic solid with a two- or three-dimensional band structure. Indeed, in the case of markedly quasi-one-dimensional complexes (CTC, KCP), a transition to the non-conducting state is observed as the temperature is reduced, while $(SN)_x$ continues to exhibit metallic properties however low the temperature.

According to Ginzburg[4], quasi-two-dimensional systems are more promising in this respect. Thus, following intercalation (the introduction of extraneous molecules into the interplanar spaces), the conductivity of many transition metal dichalcogenides changes from the semiconducting type to metallic and at sufficiently low temperatures these materials become superconductors[5]. Numerous intercalated graphite compounds are also well known[6]. The results of the intercalation of graphite by SbF_5 molecules merit particular attention; the conductivity then increases to $\sim 10^6\ \Omega^{-1}\ cm^{-1}$, exceeding by 60% the conductivity of metallic copper, while the anisotropy of the conductivity becomes greater than 10^6.[7,8] The superconducting transition in potassium-intercalated graphite observed recently[9] stimulated still further the interest in low-dimensional structures.

However, the class of systems investigated has hitherto been restricted in essence to dichalcogenides and graphite. Evidently a specific search in this field is impossible without the accumulation and systematic arrangement of knowledge concerning other low-dimensional systems which have been known for a fairly long time but whose electrophysical properties have either not been investigated at all or have been investigated at random. It is not superfluous to note that $(SN)_x$ was synthesised as early as 1910, but its unique properties remained unknown for more than 60 years. We have written this review in order to draw the attention of investigators to certain polymers which have been known for a long time, but whose investigation can lead to the expansion of our ideas concerning the electronic phenomena in solids.

II. POLYCYANOGENS

A polymeric form of cyanogen was discovered by Gay-Lussac[10] in experiments on the thermal decomposition of $Hg(CN)_2$; dicyanogen $(CN)_2$ was discovered at the same time. The composition of the polymerisation product corresponding to the formula $(CN)_x$ was soon established by Johnston[11,12], who called this polymer "paracyanogen",[12] the name which is still used. Since two polymeric forms of cyanogen are known at the present time, we shall employ this term in relation to only one of these forms.

1. The Paracyanogen Formation Reaction

There exist fairly numerous reactions leading to the formation of paracyanogen, usually as one of the products. Thus the thermolysis of dry noble metal and copper cyanides, which has been the usual preparative method for synthesising dicyanogen since the XIXth century, always leads to the formation of some paracyanogen (see the thorough review of Brotherton and Lynn[13]). Heavy metal cyanamides behave

† Kalium cyanoplatinat.

similarly[14]. Paracyanogen is formed when solid KCN interacts with the vapour of iodocyanogen[15] at the usual temperature; the reaction of chlorine with KCN at 673 K yields paracyanogen as the main product[16]. Paracyanogen arises as a side product in the pyrolysis of α-nitroguanidine,[17] *N,N'*-bis(sulphur trioxide)dicyanogen[18], cyanuric triazide[19], and melaminium hexacyanoferrate(III);[20] it is also obtained when a mixture of KCN and liquid SO_2 is stored for a long time at room temperature[21]. Considerable amounts of paracyanogen are obtained when cyanuric acid amide is acted upon by P_2O_5 [22] and in the reaction of PCl_5 with KCN or $K_4Fe(CN)_6$.[23] Paracyanogen is readily obtained on heating iodocyanogen[24] or cyanuric iodide[25] and in the interaction of CaC_2 with nitrogen[26].

The majority of the syntheses of dicyanogen[13] can apparently be used also to obtain paracyanogen *in situ*, when the reaction is carried out at a sufficiently high temperature and in a closed volume. Apart from the processes already enumerated, one may include among them the heating of dry cyanides in the presence of oxidants ($FeCl_3$, PCl_5, $HgCl_2$, etc.) and the dehydration of ammonium oxalate or oxamide under the influence of P_2O_5 or P_2S_5. Paracyanogen can also be obtained by the electrochemical oxidation of a solution of AgCN in pyridine[27].

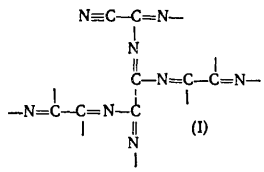
The pyrolysis of mercury and silver cyanide is used for the preparative synthesis of paracyanogen[28-30]. The total decomposition of $Hg(CN)_2$ takes place after 72 h at 623 K, after 26 h at 713 K, and after only several minutes at 873 K; the yield is higher the lower the temperature and the higher the pressure[28,31]. In order to eliminate mercury, a stream of dicyanogen is passed over the preparation at 713 K; the resulting $Hg(CN)_2$ is then distilled off. The yield of paracyanogen from AgCN is 64% at 713 K and a pressure of 6 MPa;[28] silver is removed by treatment with nitric acid. However, it was noted later[30] that the product obtained in this way can in fact consist of a mixture of $(CN)_x$ and $Ag(CN)_x$, the content of $(CN)_x$ by weight being very low. It is possible to obtain paracyanogen by heating oxamide in an evacuated vessel at 543 K; the yield reaches 30–40% when the reaction is carried out for a week and 10% in the course of two days[29]. Paushkin and coworkers[32] suggested that paracyanogen be obtained by heating oxamide or ammonium oxalate in the presence of a large excess of $ZnCl_2$ as the catalyst and dehydrating agent. After 5 h at 673 K, the yield is 30% for oxamide and 14% for the oxalate; according to X-ray diffraction data, the degree of crystallinity of the resulting polymer is high. According to Hittorf[33], the electrolysis of an aqueous KCN solution is a very convenient way of obtaining paracyanogen, giving a quantitative yield of this product. However, other workers[34] believe that this procedure does not yield paracyanogen but the polymer $(HCN)_x$ as a consequence of the hydrolysis of the dicyanogen formed initially to HCNO and HCN and subsequent rapid polymerisation of HCN. Since elemental analyses are not given in either communication, the problem still remains obscure.

Dicyanogen is known to be a chemically reactive compound—it is one of the most reactive nitriles. It is thermodynamically unstable, because its heat of formation is positive (309 kJ mol^{-1}).[13] However, in the absence of moisture and light, pure dicyanogen can be stored indefinitely at room temperature[25]. It has been found[16,31] that at atmospheric pressure and a temperature above 583 K, dicyanogen polymerises to a slight extent; this also occurs at 493 K and pressure up to 30 MPa and paracyanogen is formed even near the critical point, although very slowly[28,31]. However, these results appear to be doubtful. Chromatographically pure dicyanogen heated to 373–1473 K does not polymerise for two weeks[36]. Apparently the results of the above investigations[16,28,31] can be accounted for by the insufficient purity of the dicyanogen employed. The catalytic activity of various substances on the polymerisation of dicyanogen has been investigated. In the presence of K_2CO_3 the polymerisation begins at a temperature as low as 393 K and the same effect is produced by $NaNH_2$, but both salts begin to interact with paracyanogen as the temperature is increased. KCN, which does not react appreciably with paracyanogen, is a good catalyst at 713 K. The surface of glass exhibits only a weak catalytic effect and quartz is even less active[16]. The polymerisation of dicyanogen is catalysed by acids (CH_3COOH, HCN, CO_2), bases (NaOH, Na_2CO_3), traces of moisture and air, and metallic copper[12,35], but surprisingly, platinised asbestos has no effect[37]. When water is saturated with dicyanogen, paracyanogen appears in the solution after the latter has been allowed to stand for a long time[38] and, when dicyanogen is passed through a concentrated KOH solution, paracyanogen is precipitated immediately[38-40].

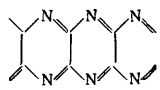
In the absence of impurities, the polymerisation of dicyanogen is induced by ultraviolet irradiation[41-45], an electric discharge[46-48], and α-particles[49-52]. Dicyanogen also polymerises in the presence of active nitrogen[53] and in the ionisation chamber of the mass-spectrometer[54,55]. Furthermore, paracyanogen is formed when gaseous hydrogen cyanide is acted upon by electric discharges[56-60] and on photolysis of carbonyldicyanogen[61,62]. The appearance of a certain amount of paracyanogen has been noted when activated nitrogen was passed over graphite[63] and on γ-irradiation of sealed tubes containing nitrogen and graphite[64].

2. The Structure and Mechanisms of the Formation of Paracyanogen

Sidgwick[65] was the first to suggest that paracyanogen may consist of a three-dimensional system (I) or a cyclic system (II):

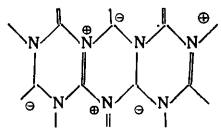


(I)



(II)

It has been established[29] that the infrared spectra of different paracyanogen specimens give rise to only one distinct absorption band at 1570 cm^{-1}, corresponding to a system of conjugated bonds. Having examined several structures, corresponding to linear (four-membered rings), ladder [six-membered condensed rings (II)], and parquet (ten-membered rings) polymers, the investigators selected structure (II). However, it has been justly noted that the band at 1570 cm^{-1} is characteristic of almost all substances containing the C=N bond and, contrary to the belief of Bircumshow et al.[29], provides no information whatever about the structure of paracyanogen. According to Rodewald[66], paracyanogen has a layer lattice of the type of graphite in which each second carbon atom is replaced by a nitrogen atom. The structural unit consists of a triazine and not a pyrazine ring. Thus the structure of paracyanogen can be described by a set of numerous valence structures of type (III) and its dark colour and high stability are due to resonance interactions. The parameters of the hexagonal layer lattice



(III)

a, c, and ρ_{theor}, determined[66] from X-ray measurements, are 0.136 nm, ~0.45 nm, and 2.0 g cm^3 respectively. The difference between the interatomic distances in paracyanogen and graphite is thus small, so that the nitrogen atoms in paracyanogen can be replaced by carbon atoms. As a result, the non-stoichiometric forms of paracyanogen never contain an excess of nitrogen and always contain an excess of carbon (see Section IV). With increase of the carbon content, the X-ray density ρ_{theor} increases, since the decrease of the parameter c is more than compensated by the increase of the parameter a. Similarly, the enthalpy of formation and the thermal and chemical stabilities increase, the colour deepens, and the electrical conductivity increases.

For a long time the attempts at a thermodynamic description of the interconversions in the dicyanogen–paracyanogen system were unsuccessful[28,37,67], because equilibrium is attained only when paracyanogen and not dicyanogen is used as the starting material. Rodewald explained this phenomenon[66]. Although the only product of the decomposition of paracyanogen is dicyanogen, the latter is not an equilibrium phase but constitutes a secondary product. On the other hand, the primary product is monocyanogen CN, which can be formed from paracyanogen as a consequence of the C–N bonds and from dicyanogen as a consequence of the dissociation of the C–C bonds. The enthalpy of the dicyanogen–paracyanogen transition, calculated by Rodewald, is close to 180 kJ. Taking into account the bond enthalpies in dicyanogen, the enthalpy of formation of paracyanogen is ~3.81 kJ. Since the heat of dissociation is 545 kJ mol^{-1}, the formation of paracyanogen never follows the shortest path $(CN)_2 \rightarrow (CN)_x$; an obligatory condition for the condensation of paracyanogen is the formation of monocyanogen: $(CN)_2 \rightleftharpoons CN \rightleftharpoons (CN)_x$. Thus monocyanogen can be converted either into dicyanogen (the formation of new C–C bonds) or into paracyanogen (the formation of C–N bonds). The second pathway is energetically more favourable, but it presupposes a fairly high partial pressure of monocyanogen.

Indeed all the results known to us confirm that Rodewald is right. It has been established[42,43] that the gas-phase photolysis of dicyanogen involves polymerisation and the quantum yield of the reaction is 3 mol einstein^{-1}. Such a low yield rules out a chain polymerisation mechanism. It has been suggested that the dissociation of $(CN)_2$ is followed by the reaction $CN + (CN)_2 \rightarrow (CN)_3$; the latter product is unstable and polymerises to paracyanogen. The thermal polymerisation of dicyanogen also begins[68,69] with the addition of the CN radical to the $(CN)_2$ molecule. These results can be interpreted only in the following way. The nucleophilic attack by the N atom of the highly polar monocyanogen on a C atom of dicyanogen should lead to a "head to tail" type of addition, so that the sequence of atoms CNCN... in the polymer is preserved. It is natural to expect that the $(CN)_3$ radical consists of a triazine ring, i.e. it constitutes the structural unit of paracyanogen#. The ease of formation of paracyanogen from substances containing the triazine ring[19,22,25] may be regarded as an additional argument in support of structure (III).

We may note that the unstable $(CN)_3^-$ ion, arising when the CN^- ion reacts with dicyanogen, has been detected even in an aqueous solution.

The radical mechanism of the formation of $(CN)_x$ is in many instances evident; the reaction proceeds on the wall at a rate limited by the rate of diffusion[20,53,63,71]. The catalytic effect shown on the polymerisation of dicyanogen by a wide variety of compounds or pressure has not so far been explained. One can only postulate that the transition state, in which the C–C bond is weakened, plays a significant role, particularly in the latter case. The doubled yield of paracyanogen[29] from $Hg(CN)_2$ compared with AgCN can possibly be accounted for by the catalytic effect of the HgCN radicals, which exist[72] at ~773 K.

Under the influence of ionising radiation, dicyanogen polymerises via an ionic mechanism[49–51,54,55]; the ions of the inert gases (He, Ne, Ar, Kr, Xe, N_2, and CO_2) then behave as catalysts. It has been noted[49] that Xe is incorporated in the composition of paracyanogen, but can be removed by heating to 623 K.

3. Chemical and Physical Properties of Paracyanogen

Depending on the methods of synthesis, paracyanogen is a powdered or porous substance with a colour ranging from brown to black and is insoluble in the usual solvents (see, for example, Refs. 29 and 52). The product obtained by Paushkin et al.[32] has a high degree of crystallinity. Paracyanogen films are also known[45]. The majority of the chemical properties of paracyanogen have already been described as early as the past century[11,12,28,38]. On heating in the absence of air, the substance begins to decompose to dicyanogen at 773 K. Complete depolymerisation occurs only at 1133 K and in the given range equilibrium is established at each temperature[28,37]; this process is accompanied by some decomposition of dicyanogen into the elements. On heating in a stream of nitrogen, paracyanogen decomposes into NH_3, HCN, and carbon[38] even at low temperatures, while in a stream of chlorine the product is chlorocyanogen[29,38].

Paracyanogen reacts fairly readily with Na_2CO_3, KOH, and soda-lime melts[29,38,73]; the initially brown melt is slowly converted into an orange-red melt and than a colourless melt; NH_3 is evolved and CN^-, CNO^-, and CO_3^{2-} ions are detected in the melt. Dicyanogen is probably an intermediate. Paracyanogen also interacts with $KHSO_4$ melt, giving rise to a substance with a deep red-brown colour. Fusion with potassium converts the polymer into KCN, but there is no reaction with sulphur and phosphorus melts. Paracyanogen does not react with aqueous solutions of alkalies, with ammonia, and with hydrocyanic acid[73], is partly soluble in 60% $HClO_4$ and in concentrated sulphuric and phosphoric acids, and is much less soluble in hydrochloric acid[29]. All these solutions have a deep colour and exhibit an intense pale-blue fluorescence on ultraviolet irradiation. Dilution with water leads to the precipitation of paracyanogen. We may note that these properties are more characteristic of colloidal solutions; the formation of colloids is in fact to be expected for a substance with structure (III).

The addition of a paracyanogen solution in H_2SO_4 to boiling concentrated HNO_3 entails the formation of a pale-yellow solution; the addition of $HgSO_4$ solution to the latter gives rise to a brown cheesy precipitate, which is converted on standing to yellow acicular crystals of "mercury paracyanate" C_4N_4OHg.

"Silver paracyanate" $C_8N_8O_2Ag$ is obtained similarly[12]. When paracyanogen interacts with hydrazine over a period of 20 h, the extent of its degradation is only 20% with formation of dark water-soluble substances[74].

An interesting property of paracyanogen is its ability to adsorb metals whose standard potentials are greater than −0.4 V from dilute aqueous solutions of their salts[75]. Here it

is easy to see an analogy with the behaviour of graphite or transition metal dichalcogenides.

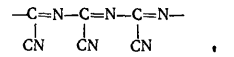
The infrared spectra of various $(CN)_x$ specimens obtained from oxamide, $Hg(CN)_2$, and AgCN contain an intense band at 1570 cm^{-1}, which has been assigned to the conjugation system[29]. After heating in air at 723 K, this band disappears and new bands appear at 640 and 1100 cm^{-1} in the case of oxamide and at 640 and 810 cm^{-1} in the case of $Hg(CN)_2$, which have not been assigned to any particular structure. If the paracyanogen precipitated from a solution in H_2SO_4 with water is redissolved in H_2SO_4, a new band appears in this spectrum at 2070 cm^{-1}, which has been assigned to the CN^- ion[29]. Since in the latter case one is dealing only with low-molecular-weight fractions, the appearance of this band can be accounted for by the protonation of some of the N atoms with subsequent addition of the counterions CN^-, arising as a consequence of the partial decomposition of paracyanogen. These data are contradicted by the results of a study[30] where the 1570 cm^{-1} band was not observed in the spectra of specimens obtained from AgCN. The authors noted an intense absorption at 1400 cm^{-1}; furthermore, the band at 2170 cm^{-1} persisted and a strong diffuse absorption was found at 3000 cm^{-1}. If there is a considerable difference between the degrees of polymerisation of the paracyanogen specimens, then the substituents at the ends of the molecules can exert a strong influence on their symmetry and hence on the relative intensities of the bands. It has been suggested that the product obtained by Wu et al.[30] is a mixture of heterocyclic substances with different degrees of polymerisation.

Measurements of the electrical conductivity of paracyanogen also differ very markedly depending on the method employed; values of 10^{-3}–10^{-4},[76] 1.7×10^{-5},[32] 2.0×10^{-6},[77] and 5×10^{-14} Ω^{-1} cm^{-1} have been obtained[78]. Paracyanogen films ~13 nm thick transmit a current of 50 mA at a field potential of 10^7 V cm^{-1}.[45] Like all polymers with a system of conjugated bonds, paracyanogen is a paramagnetic substance with a spin concentration of 5×10^{17}–1.7×10^{18} spins g^{-1}.[32,79] The study of the nature of the paramagnetic centres led to the conclusion that they consist of free radicals[79]. Measurement of the dependence of the differential thermo-e.m.f. on temperature showed[76] that paracyanogen behaves as a typical semimetal. Its conductivity is virtually independent of temperature within wide limits[32,45]. One should note particularly that measurements of the activation energy for $(CN)_x$ films in two instances yielded a value of zero, while two other measurements gave 0.16 and 0.02 eV;[45] for a disc, the corresponding value is 0.03 eV.[32] This is fully consistent with the current ideas concerning individual coplanar conjugation blocks in macromolecules, along which charged carriers migrate with a very low resistance[74,80–83]. At their ends there is an energy barrier, which the carriers must overcome in order to jump or tunnel to the next section of continuous conjugation.

In the visible region paracyanogen exhibits photoconductivity[84]; the photocurrent decreases sharply with decrease of the degree of illumination even *in vacuo*. Paracyanogen, being a catalyst of the dark oxidation of ascorbic acid, suffers a decrease of catalytic activity in the light[85]; on passing from red to white light and further to the ultraviolet region, its effect is enhanced. The study of the action of γ-rays on paracyanogen showed[86] that a dose up to 5×10^7 J kg^{-1} does not alter its physicochemical properties. However, it has been shown[77] that storage of paracyanogen for three years in the air leads to a decrease of the electrical conductivity to less than 10^{-14} Ω^{-1} cm^{-1} and a band appears in the infrared spectrum at 3220 cm^{-1} which corresponds to absorption by the OH group. Insoluble paracyanogen fractions become fully soluble in concentrated H_2SO_4.

4. Other Polymers

Paracyanogen is not the only polymeric form of cyanogen $(CN)_x$. Not so long ago, the synthesis of a linear form of polycyanogen, which is polycyanoazopolyene (IV), was reported[87]:



(IV)

The polymer was obtained by the anionic polymerisation of dicyanogen in solution in tetrahydrofuran (THF) under the catalytic influence of butyl-lithium, naphthyl-lithium, or monolithiobenzophenone and its molecular weight is in the range 200–500. The proposed structure is consistent with infrared spectroscopic data: the spectrum of the polymer contains intense bands at 2200 cm^{-1} (due to the $-C\equiv N$ groups of the conjugated system) and at 1600 cm^{-1} (due to the $-C=N-$ conjugation chain) and has been confirmed by the results[88] of electrophoretic analysis. Compound (IV) is a dark substance soluble in water and polar organic solvents and, according to potentiometric titration data, is a mono- or di-basic acid depending on the catalyst employed. The EPR spectrum of compound (IV) consists, as for paracyanogen, of a single narrow line corresponding to a spin concentration of ~10^{18} spins g^{-1}. A fine structure is not observed either at 193 K or at high dilutions, which indicate a strong delocalisation of electrons along the conjugation chain. The electrical conductivity measured in discs is close to 10^{-11} Ω^{-1} cm^{-1} at room temperature and the activation energy is ~1.9 eV.

The polymerisation of dicyanogen under the influence of electric discharges leads to polymers whose composition depends on the experimental conditions[46] and can be described by the general formula $(CN_{1-y})_x$, where $y < 1$. According to other data[48], the polymer $(C_2N)_x$, whose composition is independent of the conditions of synthesis, arises under similar conditions; the reaction is of zero order with respect to dicyanogen and the polymer. The available information about the thermal and chemical stabilities of polymers is just as contradictory[46,48]. Products with the composition $(CN_{0.9})_x$ have also been obtained in the polymerisation of dicyanogen induced by α-particles[49,50].

The pyrolysis of the tetraiodo-derivative of imidazole $C_3N_2I_4$ at 453 K entails a partial elimination of iodine and the formation of a brown polymer $(C_3N_2I)_x$; the residual iodine is split off only at 723 K, giving rise to a polymer $(C_3N_2)_x$.[73,89] Both polymers are outwardly similar to amorphous carbon. After prolonged heating, the colour changes to dark grey and the substances are converted into hard graphite-like grains. The chemical properties of $(C_3N_2)_x$ resemble those of paracyanogen[73] and on heating the polymer decomposes in accordance with the equation $(C_3N_2)_x \rightarrow (CN_2) + C$. It was established later[90] that the pyrolysis of $C_3N_2I_4$ at 723 K gives rise to a product with the ratio C : N = 1.7 still containing 0.37% of iodine. The conductivity of this polymer is 10^{-9} Ω^{-1} cm^{-1}. An increase of the pyrolysis temperature to 973 or 1073 K increases the ratio C : N from 3.2 to 6.2 and the conductivity to 2.5×10^{-2} and 0.5 Ω^{-1} cm^{-1} respectively. Triiodoimidazole behaves similarly.

Black graphite-like compounds with the compositions $(C_4HNI)_x$, $(C_4HN)_x$, $(C_4IS)_x$, and $(C_4S)_x$ have also been obtained[89] (see also Ref. 91 and 92).

It is natural to suppose that polymers of the type $(CN_{1-y})_x$ have the graphite crystal lattice and can be regarded as "copolymers" of graphite and paracyanogen. After prolonged heating, $y \rightarrow 0$, which leads to an increase of entropy and the residue consists of cryptocrystalline graphite. It

appears likely that the I atoms do not enter directly into the $(C_3N_2I)_x$ lattice but are located in the interplanar spaces, which is usual for layer compounds.

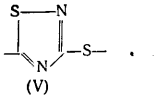
The polymerisation of dicyanogen in the presence of dry ammonia[93] or an aqueous solution of cyanide and weak acids[94,95] leads to the formation of black polymers soluble only in concentrated H_2SO_4 and decomposing at 1123–1173 K with evolution of $(CN)_2$ and HCN. Their structure has not been established. The polymers have a high heat of combustion and can be used as solid rocket fuel. Yet another cyano-polymer $(CN_4)_x$ is obtained[96] in the spontaneous polymerisation of cyanazide N_3CN; when the polymer comes into contact with water, HN_3 is evolved.

III. PARATHIOCYANOGEN

Dithiocyanogen $(SCN)_2$ was first obtained in a free state by Söderbäck[97], who established that, on rapid heating, this compound is converted, sometimes explosively, into the brick-red parathiocyanogen $(SCN)_x$. Small drops and thin layers of dithiocyanogen gradually solidify, forming a transparent brick-red resin. It was later established[98] that sufficiently pure dithiocyanogen, which melts near 298 K, polymerises on rapid heating without explosion. Boron halides catalyse the polymerisation[21]. Parathiocyanogen is one of the products of the decomposition of nitrosylthiocyanogen[21,98] and cyanazide dithiocarbonate[99], and is formed on dry heating $Hg(CN)_2$ with metal sulphides[100] and on interaction of $SOCl_2$ with AgSCN.[101] Melts of thiocyanates are readily oxidised by $FeCl_3$, $K_3Fe(SCN)_6$, $CuCl_2$, $Co(NH_3)_6Cl$, $Cu(SCN)_2$, and K_2SnCl_6, giving rise to parathiocyanogen and dithiocyanogen, which rapidly polymerise in the presence of ammonia[102]. Parathiocyanogen can be obtained also as the product of the electrochemical oxidation of melts[103–106] or solutions of thiocyanates in dimethyl sulphoxide[107]. The interaction of iodine either with melts[108] or with aqueous solutions of thiocyanates[109] is apparently the most convenient method of synthesising parathiocyanogen.

Solutions of dithiocyanogen in organic solvents are stable only at low temperatures and in the dark; on heating or ultraviolet irradiation, they precipitate a deposit of parathiocyanogen[110]. Concentrated solutions of NH_4SCN behave in the same way in the light[111,112]. It appears that in all cases one must put forward a radical mechanism of the polymerisation of dithiocyanogen. The ease of the dissociation of the S–S bond is evident; the first stage in the formation of $(SCN)_x$ from the other compounds considered is the production of SCN radicals, which rapidly and irreversibly polymerise. This is confirmed also by measurements of the magnetic susceptibility of solutions of $(SCN)_2$ by Gouy's method. It has been established[113] that freshly prepared 0.5 *N* solutions in CS_2 and $CHBr_3$ are diamagnetic. After prolonged standing, the solution in CS_2 acquires a yellow colour and becomes paramagnetic; in cyclohexane the paramagnetism appears immediately.

The structure of parathiocyanogen has not been established. Söderbäck[114] proposed the following structure (V):



(V)

However, it is known[102] that the infrared spectra of $(SCN)_x$ contain bands at 2070–2080 and 1600 cm^{-1}. The first is characteristic of organic thiocyanates and isothiocyanates and the second can be assigned to conjugated –C=N– bonds. Evidently structure (V) does not agree too well with these results. We suggest that the linear structure (VI) is more probable:



(VI) (VII)

It has been shown[105] that electrodes coated by a film of parathiocyanogen become photoactive (for example, the reduction of Cd^{2+} ions at such an electrode is accelerated when the latter is illuminated), the magnitude of the photoeffect depending on the $(SCN)_x$ deposition conditions; ageing of the precipitate leads to a decrease of the photoeffect. It has been suggested[105] that the precipitate contains initially free radicals which undergo complete polymerisation after a time; the fresh precipitate is a semiconductor. Structure (VI), which we proposed, fully explains this behaviour of the precipitate. Indeed, after a time unpaired electrons at the individual carbon atoms can recombine with formation of cross-links. Furthermore, the conductivity band in structure (VI) is 1/6 filled, which agrees with the semiconductor properties. An alternative version is structure (VII).

We may note that dithiocyanogen can be regarded as a member of the homologous series of cyanosulphanes $S_n(CN)_2$, where $n = 1–8$. All cyanosulphanes are stable only at low temperatures, vigorous polymerisation occurring on heating with formation of amorphous glassy red products of unknown structure[115]. It may be that these polymers also contain chains of type (VI).

The chemical properties of parathiocyanogen have been scarcely investigated. It is insoluble in dilute acids and alkalies and in all organic solvents, decomposing above 573 K.[114]

It has been known for a long time[116] that selenocyanogen $(SeCN)_2$ is unstable both in air and in solution. Presumably it also tends to polymerise, like $(SCN)_2$, but there is no information in the literature about its polymers.

IV. CARBON SUBOXIDE POLYMERS

1. The Formation of Polymers and Polymerisation Mechanisms

Carbon suboxide C_3O_2, discovered by Diels and Wolf[117], has a linear structure and is the simplest diketone. In the early investigations it was already noted[117,118] that a characteristic property of the suboxide is a tendency towards polymerisation. A fairly pure preparation is entirely stable at low temperatures and in the dark and even brief contact of its vapour with an incandescent platinum wire does not induce reaction[119]. The polymerisation of C_3O_2 is initiated by traces of moisture and mercury[120], phosphorus oxides[121,122], H_2SO_4, $AlCl_3$, BF_2, organic compounds[123,124], methanol, HCl, and ammonia[125]. Temperature is very important[126,127].

The principal characteristics of the polymerisation of C_3O_2 in the gas phase reduce to the following[128]. The rate of polymerisation increases with increase of temperature and pressure. The polymerisation is preceded by an induction period, the duration of which depends on the temperature but cannot be predicted for any one temperature. The reaction is heterogeneous and the induction period depends strongly on the nature of the surface of the reaction vessel, decreasing sharply if the surface is acidic (for example, in the presence of traces of H_2SO_4 or P_2O_5). If the walls are coated with paraffin, the induction period lasts more than a week. The polymerisation does not require photoinitiation and its course is the same both in the dark and in the light. The polymers obtained at room temperature are yellow, those at 373–573 K are red, and those at 673 K are violet.

Further study of the thermal block polymerisation was carried out by Blake[129], who found that the activation energies for the process are 26 and 34 kJ mol^{-1} in Pyrex and quartz vessels respectively. The duration of the induction period (ranging from minutes to several days) was satisfactorily reproducible, increasing with decrease of temperature and pressure. The reaction is of first order; the addition of CO, CO_2, O_2, NO, and C_2H_4 to the system does not affect the rate of reaction; isobutane causes a slight decrease and CCl_4 a considerable decrease of the rate of reaction and give rise to a deviation from the first order. The rate of reaction depends also on the ratio of the surface of the vessel to its volume. According to Blake[129], the presence of an induction period and the nature of the influence of additives indicate a heterogeneous reaction mechanism; in the gas phase the reaction proceeds without the involvement of free radicals, although the possibility of a surface free radical reaction cannot be ruled out. Thus the presence of the polymer does not influence the rate of reaction§, while the presence of the carbonised polymer increases the rate at low temperatures, which can be attributed to a high concentration of paramagnetic centres ($\sim 10^{20}$ spins g^{-1});[130] these centres can initiate the formation of polymerisation nuclei.

The kinetics of the thermal polymerisation of C_3O_2 subjected to preliminary irradiation by light (253.7 nm) were investigated by Smith[131]. The first order of the reaction with respect to the monomer and the polymer was confirmed, i.e. the reaction is autocatalytic. According to Smith's data, the overall activation energy on a quartz surface is 26.1 kJ mol^{-1}. Yet another confirmation of the first order of the reaction was obtained in an EPR study of the polymerisation kinetics[132,133]; the experimental activation energy in a quartz vessel was 41 kJ mol^{-1}, which is close to Blake's result[129].

The thermal polymerisation of C_3O_2 can be carried out not only in the gas phase but also in non-polar[134–140] or polar[136,141] solvents. The possible mechanism was discussed by Ziegler et al.[37], who assume that the anhydride of 3-oxoglutaric acid is an intermediate, being formed in the interaction of C_3O_2 with malonic acid. Since C_3O_2 is the anhydride of malonic acid, the presence of traces of moisture is evidently required. The use of other initiators can lead to the intermediate formation of a ketencarboxylic acid or its derivatives[125]. Later the authors[142] stated that in this mechanism the high-temperature polymerisation is possible only as an exception. A mechanism involving the initial formation of the dimer $(C_3O_2)_2$, which is an alkylketen, has also been proposed[143]. Next this keten combines in succession with fresh C_3O_2 molecules. However, it has been noted[133] that this mechanism presupposes the formation of polymers with a very high molecular weight, since the reactive alkylketen is formed at each stage, and this conflicts with experimental data.

The most justified mechanism of the thermal polymerisation of C_3O_2 has recently been proposed by Snow et al.[133] The initial stage involves the formation of an activated complex between the bent C_3O_2 molecule and the surface of the polymer or, what is more difficult, the surface of the reaction vessel. Thus the induction period is determined by the probability of the formation of such a complex. Next follows the formation of a zwitter-ionic ketocarbene capable of combining in succession with monomer molecules; the termination stage then occurs via the Wolff rearrangement and the resulting macromolecule contains two ketenyl groups.

§ This is contradicted by early data[120].

The photopolymerisation of C_3O_2 has been described by Bayes[144–146], who investigated the gas-phase photolysis in the presence of ethylene and oxygen. He suggested that, when acted upon by a light quantum, the C_3O_2 molecule gives rise to an active C_2O radical, which is capable of attacking the C=C double bonds and even C–H single bonds. This results in the formation of a polymer, allene, methylacetylene, and CO. There is also a possibility of the existence of two intermediate species with different reactivities[146,147]. In the absence of additives, the photolysis products are only $(C_3O_2)_x$ and CO. It has been established[148] that the photopolymer is analogous to the thermopolymer; the addition of O_2 to the initial monomer reduces the yield of the polymer and for the ratio $O_2 : C_3O_2 = 100 : 1$ the polymer is not formed at all. The eight-stage mechanism of photolysis proposed by Smith et al.[148] includes, apart from the formation of C_2O, the generation of an activated complex C_5O_3 with a structure of diketen-cyclopropanone. It may be[131] that the light-induced thermal polymerisation of C_3O_2 also involves the formation of C_2O.

Ultraviolet irradiation of a solution of C_3O_2 in hexane results in polymerisation[149], which gives rise to a new compound containing a carbonyl group, apparently via the reaction of a hexane molecule with the C_2O radical. Indeed the EPR spectrum of solid C_3O_2 irradiated with ultraviolet light at 77 K has a singlet signal which can be attributed to C_2O. The study of the infrared spectra of the products of the photolysis of C_3O_2 at 100 K confirms the formation of C_2O as the initial species. Next, it was suggested[150] that a tricyclic compound $C_{13}O_8$ is formed, its molecule becoming the polymerisation centres on raising the temperature.

$(C_3O_2)_x$ and CO are also formed in the gas-phase γ-radiolysis of C_3O_2.[151] Since the polymer does not collect on the surface of the reaction vessel as in thermal polymerisation but on its bottom and the addition of O_2 does not influence the yield, an ionic mechanism of the polymerisation reaction, in which the C_2O^+ ions play an important role, is evident. On γ-irradiation, liquid and solid C_3O_2 do not polymerise[152]; on heating the irradiated suboxide from 77 and 180–260 K, the rate of polymerisation is low and on further heating, it rises sharply, reaching a maximum and then falling again owing to the exhaustion of the monomer. The active centres accumulated in the low-temperature radiolysis persist even in liquid C_3O_2, which is attributed to the establishment of steric hindrance which prevents chain termination. The self-acceleration of the isothermal liquid-phase polymerisation in the absence of continuous initiation may be associated with a branched chain reaction. On irradiation of solutions of C_3O_2 in halogeno-hydrocarbons by γ-rays, fast electrons, or ultraviolet light, polymers $(C_3O_2)_x$ with a high molecular weight (>10 000) are formed, temperature and pressure having very little influence on the process kinetics and the properties of the polymers; the use of ether, CO_2, and CS_2 as solvents leads to unsatisfactory results[153]. The polymerisation of C_3O_2 can be induced also by ultrasound[154].

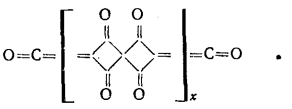
The polymers $(C_3O_2)_x$ are not formed solely from the monomer. It has been known for a long time[155] that, under the influence of a glow discharge, CO is slowly converted into $(C_3O_2)_x$ and CO_2. A thorough study[156] of this reaction showed that the polymer is formed even at 77 K and that the role of C_3O_2 in the formation of $(C_3O_2)_x$ cannot be significant. Analogous conclusions were arrived at also in the study of α-radiolysis[157] and γ-radiolysis[158] of CO; the reaction products were $(C_3O_2)_x$, CO_2, and graphite. The polymer arises from CO also as a result of ultraviolet irradiation or irradiation with fast electrons[160].

There exists a remarkable hypothesis[161], which explains the reddish colour of Mars by the presence of the polymers $(C_3O_2)_x$. Indeed the photolysis and radiolysis of CO lead to the formation of the suboxide, which rapidly polymerises. Many observations of Mars can be explained by assuming the formation of the $(C_3O_2)_x$ species on its surface and in the atmosphere[162]. It is also possible that $(C_3O_2)_x$ is the main component of the clouds of Venus[163].

In conclusion of this Section we may note that the solid red-brown substance obtained by Brodie[164] by exposing CO to the action of silent discharges (long before the work of Diels[117]) was apparently the polymer $(C_3O_2)_x$.

2. Structure and Properties

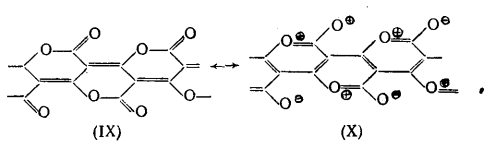
There are at present four hypotheses concerning the structure of $(C_3O_2)_x$ in the literature. The oldest is that of Hartley[165], according to which the polymerisation product is the dimer $(C_3O_2)_2$; its inapplicability from the energetic standpoint is now evident. Somewhat later Diels et al.[134] proposed structure (VIII) on the basis of the analogy between C_3O_2 and ketens. Porejko and coworkers[135,136] arrived at the same structure, justifying it with the aid of classical chemical methods and ultraviolet and infrared spectroscopy:



(VIII)

Having studied the infrared spectra, X-ray diffraction patterns, and chemical properties of $(C_3O_2)_x$, Schmidt and coworkers[138,139] proposed a completely different structure. They believe that the polymer is made up of condensed lactone and benzene rings; oxygen is located mainly in the six-membered lactone rings and at the edges of the molecule (whose diameter is close to 1 nm), there are keto- and keteno-groups. Thus the $(C_3O_2)_x$ lattice is similar to that of graphite, in which some of the C atoms have been replaced by O atoms; the distance between the planes is ~0.36 nm. However, this structure is unacceptable because 15 C_3O_2 units in it are arranged in only one possible way, as a result of which the structure cannot be built up further and less than 15 units cannot be postulated.

In order to construct a reasonable structure of the polymer $(C_3O_2)_x$, it is necessary to take into account the following factors[128]. The polymer must be formed as a result of a reaction involving C_3O_2 as the structural unit. The dimensions of the structure can be varied; all the polymers must react with water and bases to a greater or smaller extent. Since the thermolysis of polymers results in the initial evolution of CO_2, the presence of C atoms linked to two O atoms is desirable. The system of bonds must be conjugated in order to explain the intense colour of the polymers. The reaction of the polymer with ammonia should give rise to amides, whose interaction with water should lead to the appearance of carboxy-groups. A careful study[128] involving ultraviolet and infrared spectroscopy and chemical and X-ray diffraction analyses made it possible to attribute to the polymer structure (IX), which satisfies all these requirements:

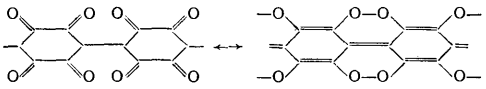


(IX) (X)

A further attractive feature of this structure is that it presupposes the existence also of an ionic pyrylium-like resonance form (X), which is highly stable and deeply coloured. Structure (IX) can be completed in different ways, but 1,2- or 2,3-addition of a C_3O_2 molecule to the ends of the macromolecule appears most likely; five-membered rings with ketenyl groups than arise.

Incidentally, an analogous structure had been proposed somewhat earlier by Ziegler on the basis of purely chemical considerations[137,167], but his work was apparently unknown to Smith et al.[128] Subsequent investigations[127,132,133,168] were consistent with structure (IX).

However, we believe that structure (IX) is not the only one possible. The resonance structures (XI)–(XII) which we put forward are entirely consistent not only with the requirements specified by Smith et al.[128] but also with infrared spectroscopic data, according to which the bands in the range 920–830 cm^{-1}, which were not identified in other studies, can be assigned to the peroxide group C–O–O–C:[169]



(XI) (XII)

In almost all the investigations which have been carried out the low stability of the polymers $(C_3O_2)_x$ was emphasised. We may note that this is true only of polymers obtained at comparatively low (less than 373 K) temperatures. Such polymers are extremly hygroscopic, water vapour altering their structure with evolution of CO_2 and the appearance in the infrared spectrum of bands due to the OH, COOH, ≡CH, and CH_2 groups; the products of the polymerisation of a moist monomer have the same spectrum[169]. The low-temperature polymers are readily soluble in water, giving red solutions. The amount of the soluble fractions diminishes with increase of the polymerisation temperature and the product obtained at 673 K is almost insoluble not only in water but also in dilute alkalies[128]. The available information about the solubility in organic solvents is contradictory. Thus polymerisation at 293 K in hexane gives rise to products which are readily soluble in ethanol but sparingly soluble in hexane; a polymer sparingly soluble in ethanol and chloroform and insoluble in hexane is formed at the same temperature in the gas phase[166]. The polymer obtained in ether[137] is readily soluble in acetone and methanol and sparingly soluble in dioxan and phenols. It has been claimed[128] that these polymers are altogether insoluble in ethanol, acetone, chloroform, carbon tetrachloride, benzene, and xylene. Effective solvents for the low-molecular-weight fractions are dimethyl sulphoxide and dimethylformamide[132,133]. At any rate it is clear that the solubility is determined mainly by the degree of polymerisation; it has been found that the polymer obtained at 373 K contains 5–10 [168] or 5–6 [133] C_3O_2 units.

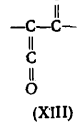
The heat of formation of $(C_3O_2)_x$ from the gaseous monomer is ~137 kJ mol^{-1}.[170] The available information about the thermal stability of polymers is also contradictory. According to Diels and Wolf[117] and Porejko et al.[135], the decomposition begins at a temperature as low as 310 K and CO_2 is evolved. Klemenc and coworkers[126,127] shift the temperature limit to ~373 K. However, careful studies[128,168,171] have demonstrated the high stability of the polymers. At 373 K the polymerisation of C_3O_2 is accompanied by the evolution of small amounts (~1%) of CO_2 and CO, which rise to 2.5 and 6% respectively at 473 and 573 K, but these gases are not the products of the thermal decomposition of the monomer or polymer. The polymer itself begins to decompose only above 573 K, whereupon its colour deepens and its oxygen content falls, but even at the temperature of red heat the polymer

nevertheless still contains a certain amount of oxygen (cf. Ciusa[89]). With increase of temperature, there is an increase of the intensity of the diffraction bands; the X-ray spectrum at 1773 K resembles that of carbon black with the particles sizes L_a = 4.5 nm and L_c = 1.4 nm [168] (cf. also Schmidt et al.[138]). The polymers obtained at 373–393 K have an extremely high surface area (~20 $m^2\ g^{-1}$) and their particle size is ~100 nm according to electron microscope data[171].

According to Mrozowski and Wobshall[130] and Schmidt et al.[139], the non-heat-heated polymer does not give rise to an EPR signal. Quite different information is contained in reports of studies[132,133,172] where the EPR spectra of the $(C_3O_2)_x$ block polymers were investigated in detail. The spectra of the polymers $(C_3O_2)_x$ obtained at 303, 333, and 363 K show an intense slightly asymmetric line, whose intensity corresponds to a spin concentration of 2.5×10^{18} spins g^{-1}; the spectrum of $(C_3O_2)_x$ obtained at 378 K shows also a second line, corresponding to a spin concentration of 2×10^{19} spins g^{-1}, the relative intensities of these two lines being different in the spectra of different specimens. The paramagnetism of the polymers obeys the Curie–Weiss law. The results of the analysis of the line form, the saturation phenomenon, the *g*-factor, and the hyperfine structure of the EPR signals suggested that the paramagnetism of $(C_3O_2)_x$ is due to electronic transitions between individual conjugation regions; the spin concentration ~2.5×10^{18} spins g^{-1} corresponds to a single spin per 600 macromolecules if one assumes that the degree of polymerisation is 6. Since contact with moisture alters the colour of the polymer, causes a gradual decrease of the intensity of the ketenyl signals in the infrared spectra, and leads to a rapid disappearance of the EPR signal, presumably the keto- and keteno-groups are responsible for the generation of relatively stable paramagnetic centres. The possible structures of the resonance forms of the radical-ions have also been published[133]. Irradiation of $(C_3O_2)_x$ with visible light leads to an additional generation of paramagnetic centres; this photoprocess is reversible[132]. The fluorescence of the soluble component of $(C_3O_2)_x$ has also been investigated.

The electrical conductivities of the polymers obtained from the monomer in ethereal solution at 293 K have been studied[140]. The observed conductivities were in the range 10^{-7}–10^{-9} $\Omega^{-1}\ cm^{-1}$ and were poorly reproducible owing to the high hygroscopicity of the polymers. The observed activation energy is close to 1.8 eV. Taking into account the method of synthesis, these results can be attributed only to low-molecular-weight oligomers $(C_3O_2)_x$, which are amorphous according to X-ray diffraction measurements[140].

There may exist also another form of $(C_3O_2)_x$, obtained when the monomer is polymerised in a polar solvent such as nitromethane[136,141]. The study of the chemical properties and infrared spectra of the polymerisation products made it possible to attribute to them the structure of a polyketone (XIII) with a degree of polymerisation of 3–4:



(XIII)

A similar product is obtained in benzene[136] in the presence of catalytic amounts of H_2SO_4 or H_3PO_4. The polymerisation mechanism is neither ionic nor radical and it has been suggested[136] that the reaction proceeds via the intermediate formation of a lactone. The density of polymer (XIII) is lower than that of the usual polymer obtained in ethereal solution (1.22 and 1.61 g cm^{-3} respectively). Polymer (XIII) consists of a very hygroscopic brown powder, which is readily soluble in dimethylformamide and alkalies. However, the dark-brown colour is characteristic also of the radiation polymers $(C_3O_2)_x$, about the structure of which there is no doubt. Since structure (XIII) does not contain a system of conjugated bonds, the deep colour is so far unexplained and the results of Porejko and Gabara[141] must be treated critically.

V. CARBON SUBSULPHIDE POLYMERS

Carbon subsulphide C_3S_2, obtained for the first time by Lengyel[173] by exposing carbon disulphide CS_2 vapour to an electric arc, is a structural analogue of the suboxide C_3O_2 and exhibits an even greater tendency to polymerise. Although C_3S_2 can be obtained also by heating CS_2 vapour to 1273–1373 K in a quartz tube[174], different modifications of Lengyel's method are still being used[175,176], but any method of synthesis involves the formation of large amounts of the polymer $(C_3S_2)_x$.

At room temperature liquid C_3S_2 polymerises spontaneously in several days and at 373 K in several minutes, while on rapid increase of temperature C_3S_2 is converted into $(C_3S_2)_x$ explosively. Solutions of C_3S_2 in CS_2 at concentrations up to 1% are stable on storage in the dark but at higher concentrations slow polymerisation takes place. This also occurs in dilute solutions in sunlight[174]. Acids and alkalies have a catalytic effect[176]. At pressures ranging from 150 to 240 MPa C_3S_2 is exothermically converted into a product fully analogous to a thermopolymer, while the polymer $(CS_2)_x$ obtained from CS_2 at a pressure of 270–450 MPa and a temperature in the range 438–553 K is slowly converted into $(C_3S_2)_x$ under the usual conditions[175]. Illumination of CS_2 with ultraviolet light (253.7 nm) also yields the polymer $(C_3S_2)_x$ together with other products[177].

It has been established[174] that the rate of polymerisation depends little on the C_3S_2 concentration and is proportional to the surface area of the vessel. The order of the reaction is close to second, but in the presence of a large surface area of the reaction vessel deviations from the second order towards the first occur. One of the possible explanations is that at the beginning two C_3S_2 molecules react with one another in the gas phase and the interaction product then polymerises on the walls of the vessel[174].

The polymer $(C_3S_2)_x$ is a black graphite-like substance insoluble in all usual solvents. The product obtained at low temperatures (below 373 K) is soluble in boiling concentrated NaOH solution, being precipitated on acidification. The infrared spectroscopic data for the polymer[175,178–181] differ somewhat from one another (in some instances[180,181] this was explained by the presence of traces of moisture during polymerisation), but the results show that the $(C_3S_2)_x$ structure is fully analogous to that of $(C_3O_2)_x$; the X-ray diffraction patterns of these polymers are also similar. On heating, the decomposition of $(C_3S_2)_x$ begins near 673 K and is accompanied by the evolution of C_3S_2 and traces of CS_2, while the residue contains carbon and sulphur[180]. According to other data[175], the monomer is not evolved on vacuum pyrolysis, only the elimination of CS_2 being observed, and the residue is a dark-red carbon like product which still contains much sulphur [~39% compared with 64% in $(C_3S_2)_x$].

The EPR spectra of $(C_3S_2)_x$ obtained at 448 K give a spin concentration of 2.5×10^{20} spins g^{-1}. Heat treatment of the polymer *in vacuo* or in an atmosphere of helium at temperatures up to 973 K has little effect on the intensity of the EPR signal, while in the presence of air it leads to an increase of signal intensity up to a temperature of ~873 K.[130] The order of magnitude of the electrical conductivity of

$(C_3S_2)_x$ is ~10^{-6} Ω^{-1} cm^{-1}.[175] It is not without interest that the reaction of sulphur with anthracene at 673 K [182] yielded a polymer containing 54% of sulphur and insignificant amounts of H and O, which is also fairly close to the elemental composition of $(C_3O_2)_x$ (see also Wibaut and Kam[92]). The electrical conductivity of this product proved to be only 3×10^{-3} Ω^{-1} cm^{-1}; no data concerning the structure are available.

VI. CONCLUSION

The polymers discussed in this review, which have a system of conjugated bonds, should be in the main semiconductors. However, their properties, particularly their electrophysical properties, have so far been inadequately investigated. Their further study and the preparation on their basis of new materials with interesting properties are worthwhile. For a specific search for such materials, it is extremely important to know the properties of the initial polymers. However, it is clear that the properties described above most probably refer only to individual specimens. For example, one cannot estimate the accuracy of the electrical conductivity measurements; it is undoubtedly low owing to the inhomogeneity of the materials and surface effects. Unfortunately there are no reliable methods for determining the degree of polymerisation of insouble polymers. Reliable characteristics could be obtained for single-crystal specimens. However, there are fundamental difficulties associated with the fact that, when coplanar blocks attain a length of 35–40 units, the coplanar inclusion of subsequent units in the chain becomes energetically less favourable than the formation of a new block unconnected to the previous ones[83]. Depending on the conditions of synthesis, the distribution of blocks with respect to the effectiveness of conjugation may change significantly.

The band structure of the polymers considered is characterised by the fact that the upper valence band and the lower conductivity band are of the π-character. Their theoretical study can therefore be based on models involving the π-electron approximation. In the simplest of the models (the Hückel model) the nature of the π-bands of $(CN)_x$ in modification (II) has been discussed[183]. It has been shown that in such systems the alternation of bond lengths and hence of resonance integrals is insignificant. It is more important that the difference between the electronegativities of the C and N atoms, described by the difference between their Coulombic integrals, makes the main contribution to the energy gap of the polymer with a fully filled π-band. The electronic structure of $(CN)_x$ in modifications (II) and (IV) has also been calculated within the framework of the extended Hückel method using crystal orbitals[184]. The application of this model to modification (II) resulted in the overlap of the lower vacant π-band (conductivity band) and the upper occupied σ-band (valence band), formed by the lone electron pairs of nitrogen, which give rise to a ground state of the metallic type.

In discussing these results one should not, incidentally, neglect the fundamental defects of the method, which have been pointed out, for example, by Dewar[185] and which are particularly pronounced for heteroatomic systems of the type under consideration. It may be that the result obtained is an artefact of the Hückel model. The fact that $(CN)_x$ with structure (IV) exhibits in the same calculations a considerable stability and an energy gap of ~1.4 eV of the semiconductor type is in better agreement with experimental results. The calculation[184] on the parquet polymer $(C_3N)_x$ also led to a metallic conductivity, since, as a consequence of the odd number of π-electrons in the unit cell, the upper valence π-band is partly filled. Clearly, paracyanogen (III) should exhibit, within the framework of this model, a metallic character like graphite, which is fully consistent with experimental data[76].

According to modern ideas concerning the electronic structure of polyconjugated polymers[186], the ordered system made up of the graphite network by the replacement of certain carbon atoms by boron or nitrogen atoms should be ferromagnetic, since its total spin in the ground state is infinite. Difficulties associated with the creation of polymeric ferromagnetic materials of this kind have recently been noted by Buchachenko[187].

The band structure of the remaining polymers deals with in the review has not apparently been studied. It is clear from general considerations that the difference between the Coulombic integrals for the C, O, and S atoms should lead to the absence of overlap of the valence and filled bands and hence to semiconducting properties of the polymers, and the energy gap in the case of $(C_3S_2)_x$ should be smaller than in the case of $(C_3O_2)_x$.

It is appropriate to point out a number of considerations concerning specific ways of increasing the electrical conductivity of the polymers considered. Among purely physical methods, one may indicate the application of a high pressure[188], which, by reducing the internuclear distances and by increasing the overlap of the atomic orbitals, leads to the overlap of a number of bands, as a consequence of which a typically semiconducting system becomes metallic. A remarkable example of this kind is provided by elemental sulphur[189]. In principle, there is then a possibility of transitions to a structure with another crystal lattice. However, chemical methods are more effective and easier to apply, for example the intercalation already mentioned. The scope of this method is extremely wide, which can be illustrated by the following example. When partly oriented films of polyacetylene $(CH)_x$ are doped with donors of acceptors (Na, I_2, AsF_5, etc.), the conductivity increases from 10^{-10}–10^2 Ω^{-1} cm^{-1}, i.e. by twelve orders of magnitude, and materials of *p*- and *n*-types are obtained[190]. The results of the intercalation of hexagonal boron nitride $(BN)_x$, which is converted from a typical insulator to a conductor following the introduction of $S_2N_6F_2$, are even more striking[191].

Certain conjugated polymers have already found applications as the working materials of thermoresistors and tensotransducers, many parameters of which are superior to those of the usual industrial specimens[81]. A high-quality *p*–*n* junction with very effective rectifying properties has been prepared[192] from $(CH)_x$ films of different types. Thus one may expect interesting electrophysical properties of intercalated polymers, to the discussion of which this review has been devoted, and in the future new materials important for modern technology may be obtained. Advances in this field can depend to a large extent on the preparation of single-crystal specimens of the corresponding polymers.

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Phenomenological Sorption Thermodynamics

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The thermodynamics of sorption of pure substances and of mixtures from the vapour or the liquid phase on sorbents of different types are discussed. The stoichiometric theory of adsorption and the osmotic theory (based on the vacancy solution model) are analysed in detail, as well as the most recent advances in the theory of volume filling of micropores. The following problems are examined: the validation of the model, and of the choice of components of the sorption solution, the methods of calculating the appropriate activity coefficients, the internal thermodynamic consistency of data on adsorption from the vapour and the liquid phase, and the prediction of equilibrium adsorption characteristics from the smallest possible amount of experimental data. Capillary phenomena are examined from the standpoint of maximising the information on the pore structure of the adsorbent. 80 references.

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I. INTRODUCTION

The increasingly wide application of sorption processes in chemical industry has been responsible for recent developments in the study of adsorption, and in particular of the thermodynamic theory of adsorption. The control and optimisation of these processes, the preparation of adsorbents offering the required selectivity towards certain components of the mixture, and the identification of the mechanism of adsorption–catalytic processes have created a need for still further developments in theoretical studies of adsorption.

One of the most important theoretical problems is to develop methods of predicting the equilibrium characteristics of adsorption in one-component and multi-component systems, because the empirical approach to achieving selectivity in adsorption systems (and thus making the systems more effective and economically attractive) is laborious and impractical when the number of mixtures to be extracted, purified, or separated is very large. In principle this problem can be solved by molecular–statistical thermodynamics.

Many recent experimental and theoretical papers have dealt with intermolecular interactions in sorption systems, and with the study of the physical and physicochemical

properties of adsorbents and adsorbed molecules by modern methods of analysis. However, the complexity of the problem is such that rapid progress cannot be expected by this approach. Far more useful advances have been made in the developments of a strict phenomenological theory of adsorption thermodynamics usable in conjunction with empirical rules or non-thermodynamic considerations suggested by simple, approximate models of sorption systems.

In this review we shall examine recent achievements in that type of work. No attempt will be made to cover the literature exhaustively, but we shall try instead to clarify the present position of the thermodynamic theory of adsorption by referring to published information as required.

The symbols used in this review have their conventional meaning (unless accompanied by a statement to the contrary). We shall also use the following additional symbols:

n_i, c_i, x_i, γ_i are the number of moles, the concentration (mole litre^{-1}), the mole fraction, and the activity coefficient of the stated component in the bulk phase (the tilde sign ~ denoting the liquid solution when a vapour and a liquid bulk phase can coexist, e.g. $\tilde{c}_i$, etc.);

$\bar{n}_i$, $\bar{c}_i$, $\bar{x}_i$, θ_i, $\bar{\gamma}_i$, $\bar{\varphi}_i$, are the number of moles, the concentration (mole kg^{-1}), the mole fraction, the surface coverage, the activity coefficient, and the full chemical potential of the components of the sorption solution (the subscript R denotes the adsorbent, for example $\bar{c}_R$ is the concentration of the adsorbent); c_{is}, γ_{is}, $\tilde{c}_{0i}$, $\bar{c}_{0i}$ are the concentration (mole litre^{-1}) and the activity coefficient of the saturated vapour and of the pure liquid component and the concentration (mole kg^{-1}) of the sorption solution when saturated with the stated component; s_i, s_R, and s are the molar volumes or areas of the components of the sorption solution;

σ is the surface tension or internal pressure;

W *and* W_0 are the surface (or volume) and the specific surface (or volume) of the macroporous or microporous sorbents;

$\bar{v}_{0i}$ is the molar volume of the liquid adsorbate at the given temperature;

K_i and $\bar{K}_i$ are the equilibrium coefficient and the thermodynamic equilibrium constant for the adsorption of the i-th component;

α, K, and $\bar{K}$ are the separation coefficient, the equilibrium coefficient, and the thermodynamic equilibrium constant for the adsorption of a binary mixture;

g_i is the osmotic coefficient of component i in the sorption solution;

β_i, β, and $\beta_i(af)$ are the stoichiometric coefficients for the individual and the exchange adsorption, and the affinity coefficient of the theory of volume filling of micropores (TVFM);

α_i is the thermal expansion coefficient of the components of the sorption solution in the TVFM;

E_0 is the characteristic free energy of adsorption of the standard vapour in the TVFM;

r is the equivalent radius of the mesopores;

t and t_e are the mean square thickness of the adsorption layer in the mesopores without and with the correction (respectively) for the effect of the sorption field of the sorbent;

ω is the parameter of Tolman's equation.

II. THE SORPTION SOLUTION MODEL

Two methods of describing adsorption systems thermodynamically are known: the Gibbs surface excess method[1] and the finite thickness layer method (or, more exactly, the total content method)[2]. In the Gibbs method the real structure of the adsorption phase is ignored. Therefore the thermodynamic functions determined from the experimentally measured excess quantities apply to the sorption system as a whole and cannot be used to analyse the distribution of volume phase and of sorption phase in the adsorbents, and the thermodynamic properties of the latter. For this reason modern theories of adsorption have tended to rely on the finite thickness layer method.

In the thermodynamic analysis of sorption systems a distinction is often made between adsorption in the surface layer (macroporous sorbents) and in the volume of micropores (microporous sorbents). In a critical analysis of this approach[3] a new function (Φ) was introduced to describe both processes within the same thermodynamic model. As the present writer recently pointed out[4], the properties of both these sorption phases are similar in many ways[3,4], though they differ very substantially from those of ordinary bulk phases: the pressure in the plane of the surface layer of the bulk sorption phase is different (at least, in some directions) from the total pressure P in the system. Hence, in both cases[1,4,5] the fundamental equations should include the term σdW to allow for the additional work of formation of the surface layer (where σ is the surface tension and W is the area of the surface) or of the "volume" sorption phase in the micropores (where σ is the internal pressure and W is the volume of the sorption phase):

$$\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V + \sum_i \mu_i\,\mathrm{d}n_i + \sum_i \bar{\varphi}_i\,\mathrm{d}\bar{n}_i + \sigma\,\mathrm{d}W, \tag{1}$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P + \sum_i \mu_i\,\mathrm{d}n_i + \sum_i \bar{\varphi}_i\,\mathrm{d}\bar{n}_i + \sigma\,\mathrm{d}W \tag{2}$$

so that

$$-S\,\mathrm{d}T + V\,\mathrm{d}P + \sum_i n_i\,\mathrm{d}\bar{\varphi}_i + W\,\mathrm{d}\sigma = 0. \tag{3}$$

The full chemical potentials of the components of the sorption solution should be written[1,5] as

$$\bar{\varphi}_i = \bar{\mu}_i^0(T, P) + RT\ln\bar{c}_i\bar{\gamma}_i - \int_0^\sigma s_i\,\mathrm{d}\sigma = \bar{\mu}_i - s_i\sigma, \tag{4}$$

$$\bar{\varphi}_i = \bar{\mu}_i^0(T, P) + RT\ln\bar{x}_i\bar{\gamma}_{ix} - \int_0^\sigma s_i\,\mathrm{d}\sigma = \bar{\mu}_i - s_i\sigma. \tag{5}$$

The molar areas or volumes (s_i) of the components of the sorption solution depend (in general) on the composition of the solution. However, since the dependence is usually not very marked, and the form of the relevant function is not known, we can adopt the rigid sorption solution model (i.e. $s_i = \text{const}$) without affecting the thermodynamic validity of the argument. Any deviation from the assumed model can be allowed for by choosing an appropriate activity coefficient. By this approach (which is currently favoured by most workers) correct use can be made of the right-hand side Eqns.(4) and (5). We note that in the calculation of $\bar{\gamma}_i$ and $\bar{\gamma}_{ix}$ reference (standard) states differing by a factor of $\bar{c}_{0i}$ are usually used:

$$\bar{\gamma}_i,\ \bar{\gamma}_{ix} \to 1 \text{ for } \bar{c}_i \to \bar{c}_{0i}, \text{ i.e. } \bar{x}_i \to 1, \tag{6}$$

whereas $\bar{\gamma}_{ix} = \bar{\gamma}_i\bar{c}_0$ (where $\bar{c}_0$ is the total concentration of the solution), which leads to a formal difference between the numerical values of the standard parts of the chemical

potentials and of the standard thermodynamic functions derived from them[6-8].

Another important property of the sorption phase is its finite size (implicit in the finite thickness layer model). Thus, the sorption solution is a phase of limited capacity with respect to the overall combination of components of the solution. Since the inhomogeneous region at the contact between two phases extends, strictly speaking, to the whole volume[5], the fundamental problem in the total content method is a thermodynamically correct choice of the size of the sorption phase (thickness, in the case of adsorption on macroporous systems, and volume, in the case of sorption in micropores).

In the sorption of gases or vapours the excess adsorption quantities are almost identical to the corresponding total contents of components in the sorption phase. Hence the model phase can be chosen with adequate precision on the basis of the adsorption isotherm and of physically acceptable data on the effective size of the adsorbed molecules (monlayer thickness for the sorption of gases on macroporous sorbents, and micropore volume for the sorption of gases and vapours in micropores). The sorption of vapours in macropores is complicated by multimolecular adsorption and capillary condensation phenomena, and requires a special thermodynamic analysis.

Sorption from liquid solutions is a far more complex problem, because in this case the experimental data can be used reliably to calculate only the minimum capacity of the sorption phase[5,9], and this cannot be a basis for a correct choice of the size of the phase[9,10]. An interesting method for the thermodynamically correct choice of a sorption phase model in this case was proposed by Larionov[9].

1. The monolayer capacity $\bar{c}_{i(M)}$ or micropore volume $\bar{c}_{i(W)}$ is determined experimentally. Critical studies[9,10] of the methods of determining these quantities for the sorption of vapours and of liquid solutions suggest that the most reliable results are obtained by comparing data for the sorption of pure vapours with data for the sorption of their binary liquid solutions.

2. The size of the sorption phase is obtained by multiplying the $\bar{c}_{i(M)}$ or $\bar{c}_{i(W)}$ values thus obtained by the arbitrarily chosen factor k.

3. Using the experimental excess sorption isotherm of the binary liquid solution the changes in σ or in the thermodynamic wetting functions attending the transfer of the sorbent wetted with one of the components to a solution of composition $\tilde{x}_1$ are calculated by the Gibbs and the total content method. The Gibbs method, being free from any model assumptions, yields the true values of the change in the thermodynamic functions of the sorption system. In the calculation by the total content method the result obtained depends on the chosen model, i.e. on the value of k. By varying k so as to make the two sets of results coincide a thermodynamically correct model of the sorption solution is obtained.

Larionov applied this method of analysis to a large number of adsorption systems[9,11,12], and he showed that in the case of microporous sorbents the volume of the micropores is a good approximation to the volume of the sorption phase. With macroporous sorbents the best approximation is given by the monolayer volume, or occasionally by the volume of two or three layers. Thus, even in the case of sorption from liquid solutions the model of a rigid layer of finite thickness is thermodynamically justified.

The choice of components of the sorption solution is an important part of the construction of the model of the sorption phase[3,4,6,13-17]. The problem consists in defining, within the thermodynamic meaning of the term, a set of components which allows the required thermodynamic relationships to be set up in the simplest way for different sorption systems (both one-component and multi-component).

If the components of the sorption solution are identified with the substances in the bulk phase (A, B, ...), and the sorbent is not explicitly treated as a component of the sorption solution, the role of the sorbent is limited to the creation of an adsorption force field. In this case the equilibrium conditions in a closed system become (P, T = const)

$$\bar{\varphi}_i = \mu_i. \tag{7}$$

This choice of components is thermodynamically correct, but not always convenient. For example, from (5) and (7) we obtain the adsorption isotherm equation

$$\bar{c}_i\bar{\gamma}_i = c_i\gamma_i \exp[(\mu_i^0 - \bar{\mu}_i^0 + s_i\sigma)/RT], \tag{8}$$

which contains the experimentally inaccessible quantity σ. Of course, by solving Eqn.(8) simultaneously with the Gibbs adsorption equation for a layer of finite thickness

$$\sigma = -\frac{RT}{W_0}\int_0^{c_i}\sum_i \bar{c}_i\, d\ln c_i\gamma_i, \tag{9}$$

we can eliminate σ from Eqn.(8) and obtain a general form of the adsorption isotherm equation. However, this approach presents mathematical difficulties, due to the complicated dependence of σ on the composition of a multi-component sorption solution containing molecules of different size, and to the absence of an analytical expression of the type of $\bar{c}_i = f(c_i\gamma_i)$.

Complications can arise also in the analysis of systems showing evidence of chemisorption, since in this case we cannot assume that the component remains chemically identical in the two phases in equilibrium. We should stress that the stipulation commonly made in this case that the sorbent must be "inert" (i.e. that $\bar{\phi}_R$ = const) is thermodynamically incorrect, since [as we see from Eqns.(4) and (5)] σ varies during sorption. The errors caused by this assumption are discussed in Ref.14.

In the thermodynamic stoichiometric theory of adsorption (STA) developed by the present writer[4,6,13,18-22] the components of the sorption phase are taken to be the complexes formed by the adsorbate species with the sorption centres and the free sorption centres of the sorbent (AR_{s_A/s_R}, BR_{s_B/s_R}, R), whose mass is divided into the number of moles ($\bar{n}_R$) so that a molar surface or volume (s_i, s_R) can be associated with each mole of the components, and for W = const we have

$$s_i = W/\bar{n}_{0i} = W_0/\bar{c}_{0i},\quad s_R = W/\bar{n}_{0R} = W_0/\bar{c}_{0R}, \tag{10}$$

and since the sorption solution is always saturated with the sum of the components we also have

$$\sum_i s_i\bar{n}_i + s_R\bar{n}_R = W, \tag{11}$$

$$\sum_i s_i\, d\bar{n}_i + s_R\, d\bar{n}_R = 0. \tag{12}$$

[Since the value of $\bar{c}_{0R}$ is unknown we cannot evaluate s_R numerically from the expressions (10)].

This choice of components is consistent with the physically possible occupancy of several sorption centres by a sorbate molecule, it treats the adsorbent explicitly as one of the components of the system, and it is thermodynamically strict, whatever the magnitude of the adsorbate–absorbent interaction (i.e. it is equally correct whether the adsorption energy is close to the energy of a chemical bond, as in

chemisorption, or whether it is a weak dispersion interaction as in the adsorption of inert gases on graphitised carbon). It allows a fairly simple description of adsorption equilibria in different sorption systems (involving localised or delocalised physisorption or chemisorption) for the one-component or multi-component sorption of molecules of different size from bulk phases of any kind.

We should stress that Eqns.(11) and (12) apply when all the sorption centres are equally accessible to the adsorbate molecules, i.e. when molecular sieve effects are absent. If, on the other hand, in a two-component adsorption system the sorption volume W_A is available to A molecules and the sorption volume W_B to B molecules, with $W_B > W_A$, Eqns.(11) and (12) will apply only to the volume W_A, and similar expressions can be written for the adsorption of component B in the volume $W_B - W_A$.[18,21]

Simultaneous solution of Eqn.(2) (for P, T = const) and Eqn.(12) gives the basic equations of the STA:[4,6,13]

$$(\bar{\varphi}_A - \mu_A)/s_A = (\bar{\varphi}_B - \mu_B)/s_B = \ldots = \bar{\varphi}_R/s_R, \qquad (13)$$

or, using Eqn.(5)

$$(\bar{\mu}_A - \mu_A)/s_A = (\bar{\mu}_B - \mu_B)/s_B = \ldots = \bar{\mu}_R/s_R. \qquad (14)$$

Thus the choice of components for the sorption solution adopted in the STA allows us to treat adsorption processes as quasi-chemical addition reactions ($\beta_i = s_R/s_i$):

$$\beta_A A + R \rightleftarrows \beta_A AR_{1/\beta_A} \text{ etc.} \qquad (15)$$

or exchange reactions ($\beta = s_A/s_B = \beta_B/\beta_A$):

$$A + \beta BR_{1/\beta_B} \rightleftarrows AR_{1/\beta_A} + \beta B \text{ etc.} \qquad (16)$$

and therefore it makes the well developed methods of chemical thermodynamics available for the thermodynamic description of adsorption processes. On the other hand the properties of sorption solutions can be discussed in terms of the most recent advances in the theory of solutions of different-sized particles.

In the osmotic theory of adsorption (OTA) developed by Bering, Serpinskii, and others[15-17] the components of the sorption solution are adsorbate molecules and vacancies, which are identified with elements of free space in the sorption volume of micropores or in a surface layer of finite thickness. This choice of components is in many ways analogous to the previous variant, but in this case the equilibrium phases contain at least two components, which allows the methods of the osmotic theory of solutions to be applied to the analysis of one-component adsorption. Since the model assumes that in the sorption of pure substances $s_i = s_* = W_0/c'_{i,\max}$ (where s_* is the molar volume of the vacancies) on changing to multi-component adsorption we have $s_* \neq$ const, and Eqn.(12) for W = const is replaced by

$$\sum_i s_i \, d\bar{n}_i + s_* \, d\bar{n}_* + \bar{n}_* \, ds_* = 0, \qquad (17)$$

where the variations ds_* are many-valued functions of the composition of the sorption solution. This makes necessary the use of special algorithms in the thermodynamic analysis of these systems.

We also note that in the case of one-component adsorption imposing the condition $s_i = s_*$ on the model may perturb the real physical description of the solution, since according to the general statistical theory of binary solutions[6] we can write for $\bar{\gamma}_i$

$$RT \ln \bar{\gamma}_i = RT\bar{c}'_R(s_R - s_i) + (\bar{c}'_R)^2 s_R (s_R s_i)^{1/3} \Delta U_{i-R} \qquad (18)$$

(where $\bar{c}'_R$ is in mole litre^{-1}, and the subscript R is analogous to $*$), and any deviation from ideality (i.e. any deviation of $\bar{\gamma}_i$ from unity) should be associated with changes in the intermolecular interactions in solution ΔU_{i-R}, whereas such deviations could result simply from the difference in size of the component molecules with $\Delta U_{i-R} = 0$. The latter feature is, of course, entirely irrelevant to a formal thermodynamic analysis.

A very important aspect of this model is the fact that the vacancy solutions are in a state of osmotic equilibrium, i.e. the chemical potential of the solvent (vacancies) in the sorption phase is equal to the chemical potential of the pure solvent (vacancies in a vacuum). Therefore, using (5), we have[15,16]

$$\mu_* = \bar{\mu}^0_*(T, P) + RT \ln \bar{x}_* \bar{\gamma}_* - s_* \sigma = \mu^0_*(T, P). \qquad (19)$$

Since $\bar{\mu}^0_* = \mu^0_*$, and $\bar{x}_* = \bar{c}_*/\bar{c}_{i,\max} = \bar{\theta}_* = 1 - \bar{\theta}_i$, it follows from (19) and (10) that for one-component adsorption

$$\sigma W_0 = \bar{c}_{i,\max} RT \ln [(1 - \bar{\theta}_i)\bar{\gamma}_*]. \qquad (20)$$

The advantage of the OTA vacancy model is not only that the theory of bulk solutions can be applied to the sorption phase, but also that a general adsorption isotherm equation can be obtained relatively simply (without the need to integrate the Gibbs adsorption equation) by solving Eqns.(20) and (7) simultaneously after writing the latter in a form appropriate to the adsorbate A:[17]

$$\mu^0_A + RT \ln c_A \gamma_A = \bar{\mu}^0_A + RT \ln \bar{x}_A \bar{\gamma}_A - s_A \sigma. \qquad (21)$$

We note that the chemical potential of the sorbent changes during sorption, but $\bar{\phi}_*$ according to (19) remains constant for all values of $\bar{\theta}_i$. Therefore the vacancies cannot be treated as formally analogous to the sorbent, and the latter is not one of the components of the sorption solution in the OTA model.

To conclude this discussion of the model of the sorption solution we need to examine the precise definition of the limiting adsorption value.

If the $\bar{c}_{0i}$ values are found by extrapolating the linearised adsorption isotherm equations to $c_i \to \infty$ (for gases) or to $c_i = c_{is}$ (for a saturated vapour) they give only an approximate indication of the limiting adsorption under the given conditions, since the equations do not apply for $\bar{\theta}_i \to 1$. These values are termed apparent limiting adsorptions to distinguish them from the true values ($\bar{c}'_{0i}$) obtained by direct physical measurements (for example, at $c_i = c_{is}$). The latter values are of the utmost importance in studies of the physical properties of sorption solutions. In the case of delocalised adsorption both $\bar{c}_{0i}$ and $\bar{c}'_{0i}$ are, of course, functions of temperature.

The proponents of the osmotic theory of solutions[14-17] suggest that the limiting adsorption of a gas, vapour, or liquid should be treated as the maximum achievable adsorption, consisting of the maximum possible number of sorbate molecules close-packed in the sorption volume:

$$\bar{c}_{i,\max} = W_0/\bar{v}_{i,\min}. \qquad (22)$$

An obvious disadvantage of introducing $\bar{c}_{i,\max}$ is the need to evaluate this quantity from adsorption measurements. This difficulty was satisfactorily overcome[17], however, by calculating the molar volume of the substance subjected to maximum compression ($\bar{v}_{i,\min}$) from the parameter σ_∞ (the intermolecular interaction potential).

The use of the maximum adsorption values offers the obvious advantage that these quantities are independent of temperature, but the calculation of $\bar{c}_{i,\max}$ by Eqn.(22) is complicated and indeterminate to some extent, and the worth-whileness of introducing the quantity $\bar{c}_{i,\max}$ into the analysis of conventional adsorption equilibria requires

further discussion. Of course, the validity of the thermodynamic analysis is unaffected by whether the chosen model of the sorption solution does or does not rely on the quantities $\bar{c}_{0i}$ and $\bar{c}_{i,max}$.

We shall now briefly examine recent developments in the thermodynamic theories of sorption based on different models of the sorption solution.

III. THE STOICHIOMETRIC THEORY OF ADSORPTION

1. Adsorption of Pure Substances

From Eqn.(13) or (14), using Eqn.(4), we can easily obtain a general isotherm equation for one-component adsorption[6,22]:

$$\bar{K}_A = \beta_A (\bar{c}_A\gamma_A)^{\beta_A}/(c_A\gamma_A)^{\beta_A}(\bar{c}_{0A} - \bar{c}_A)\,\bar{\gamma}_R = \bar{K}_A^{*}\bar{\gamma}_A^{\beta_A}/\bar{\gamma}_R. \qquad (23)$$

Since $d\bar{c}_A = -\beta_A d\bar{c}_R$, we can write (for P, T = const)

$$\bar{c}_A\, d\ln\bar{\gamma}_A + \bar{c}_R\, d\ln\bar{\gamma}_R + (1 - 1/\beta_A)\, d\bar{c}_A = 0 \qquad (24)$$

and eliminate $\bar{\gamma}_R$ from (23):

$$\left(\frac{\bar{K}_A}{\beta_A \bar{c}_{0A}^{\beta_A - 1}}\right)^{1/\beta_A} = \bar{K}'_A = \frac{\bar{c}_A\bar{\gamma}_A}{c_A\gamma_A\,(\bar{c}_{0A} - \bar{c}_A)} \exp\left[\int_0^{\bar{c}_A}\left(\frac{\bar{c}_A}{\bar{c}_{0A} - \bar{c}_A}\right) d\ln\bar{\gamma}_A\right]. \qquad (25)$$

From the general equations (23) and (25) we can obtain special formulae for specific types of $\bar{\gamma}_i = f(c_i)$ relationship, chosen on the basis of various theories of solutions (e.g. the Hill equation, the Fowler and Guggenheim equation, etc.[22]). The following three cases are the most interesting.

1. For ideal adsorption (γ_A, $\bar{\gamma}_A$, $\bar{\gamma}_R = 1$, and therefore $\beta_A = 1$) Eqns.(23) and (25) reduce to the Langmuir equation.

2. If the sorption solution consists of non-interacting particles of equal size [$\Delta U_{i-j} = 0$, Eqn.(18)] we have

$$\bar{\gamma}_A = \exp\left[\frac{\bar{c}_R\,(s_R - s_A)}{W_0}\right] = \exp\left[\frac{\beta_A - 1}{\beta_A \bar{c}_{0A}}(\bar{c}_{0A} - \bar{c}_A)\right], \qquad (26)$$

and Eqn.(25) reduces to

$$\bar{K}'_A = \bar{K}_A \exp\left[\frac{\beta_A - 1}{\beta_A}\right] \Big/ \beta_A = \bar{c}_A^{\beta_A}/(c_A\gamma_A)^{\beta_A}(\bar{c}_{0A} - \bar{c}_A), \qquad (27)$$

which can be linearised (for $\gamma_A = 1$) in order to evaluate β_A.

Eqn.(27) has been applied[19] to published data claimed to be in satisfactory agreement with the Langmuir isotherm. Values of β_A differing significantly from unity were obtained, and it was shown that Eqn.(27) offers a better description of the experimental results. Exactly as required by Eqn.(10), the quantities $\beta_A : \beta_B : \beta_i$ were found to be in the same ratio as $\bar{c}_{0A} : \bar{c}_{0B} : \bar{c}_{0i}$, a positive confirmation of the validity of the basic assumptions of the STA. Hence the β_i values could be calculated from the expressions

$$\beta_i = \beta_j \bar{c}_{0i}/\bar{c}_{0j}. \qquad (28)$$

If an adsorbate to which Eqn.(27) is strictly applicable on the given sorbent cannot be found, the parameter β_j for any adsorbate is evaluated approximately by Eqn.(27) and all the other β_i values are found by Eqn.(28).

3. As was pointed out by Bering and Serpinskii[15], in the sorption of various adsorbates on microporous adsorbents the $\bar{\gamma}_i = f(\bar{c}_i)$ relationship can often be written

$$\bar{\gamma}_A = \bar{c}_A^{g_A - 1}, \quad \bar{\gamma}_R = \bar{c}_R^{g_R - 1}, \qquad (29)$$

where g_A and g_R are constant for $0 < \bar{c}_i < \bar{c}_{0i}$, and $g_i \to 1$ for $\bar{c}_i \to \bar{c}_{0i}$. Inserting (29) into (25) leads to the Kisarov equation[22] [since according to Eqn.(24) $g_R = \beta_A g_A$]:

$$\bar{c}_A = (\bar{K}_A/\beta_A)^{1/g_R}\bar{c}_{0A}c_A^{1/g_A}/[1 + (K_A/\beta_A)^{1/g_R}c_A^{1/g_A}], \qquad (30)$$

and after replacing $\bar{c}_{0A}$ by $\bar{c}_{A,max}$ it leads to the corresponding equation of the osmotic theory of adsorption[15]. In spite of a statement to the contrary in Ref.15, Eqn.(30) describes a more general case of sorption solution, with components of unequal size ($\beta_A \neq 1$).

If the special forms of Eqn.(25) cannot be applied satisfactorily to specific experimental results it becomes necessary, in order to use (23) or (25), not only to determine β_i from Eqn.(27) or (28) but also to evaluate $\bar{\gamma}_i(\bar{c}_i)$ and $\bar{K}_i$ from the experimental data. This problem has been resolved[8] by simultaneous solution of (23) and (24) using Eqn.(6) for the standard states.

If the temperature dependence of the adsorption is known over small temperature ranges, in which β_i can be assumed to be independent of T, full thermodynamic information on the sorption system can be extracted from the conventional equations of chemical thermodynamics. In this case it is advantageous to replace $\bar{c}_{0i}$ by $\bar{c}_{i,max}$ in Eqn.(10) and in the following equations, thus making β_i strictly independent of temperature.

2. Adsorption of Mixtures

To simplify the treatment we shall confine the discussion to the adsorption of binary mixtures. In this case we obtain from (13) or (14) and (4) general adsorption isotherm equations in the form of[6,22]

$$\bar{K} = \frac{\bar{c}_A\bar{\gamma}_A\,(c_B\gamma_B)^{\beta}}{c_A\gamma_A\,(\bar{c}_B\bar{\gamma}_B)^{\beta}} = K\frac{\bar{\gamma}_A\bar{\gamma}_B^{\beta}}{\gamma_A\bar{\gamma}_B^{\beta}} = K'\frac{\bar{\gamma}_A}{\bar{\gamma}_B^{\beta}}, \qquad (31)$$

$$\bar{K}_A = \frac{(\bar{c}_A\bar{\gamma}_A)^{\beta_A}}{(c_A\gamma_A)^{\beta_A}\,(\bar{c}_{0A}/\beta_A - \bar{c}_A/\beta_A - \bar{c}_B/\beta_B)\,\bar{\gamma}_R}. \qquad (32)$$

The parameter β is easily determined according to (10) or (16):

$$\beta = \bar{c}_{0B}/\bar{c}_{0A}. \qquad (33)$$

If molecular sieve effects are present we proceed as in Refs.18 and 21. We should stress that Eqn.(31) applies for any level of coverage of the sorbent by the sum of the adsorbates ($\bar{\theta}_{A+B}$), and also for multi-component adsorption. In the latter case it offers greater generality than other similar equations proposed earlier by various authors for the sorption of binary liquid solutions (i.e. for $\bar{\theta}_{A+B} = 1$). For specific types of $\bar{\gamma}_i = f(\bar{c}_i, \bar{c}_j)$ relationship we can easily obtain from (31) or (32) the isotherms for adsorption from binary mixtures proposed by Frumkin, Damaskin, and others[22].

In the special case of non-interacting particles of different size [$\Delta U_{i-j} = 0$ in an equation analogous to (18)] the quantities $\bar{\gamma}_i$ in a three-component sorption solution can be defined by analogy with (26), and Eqn.(32) then becomes

$$\bar{K}'_A = \bar{K}_A e^{\beta_A - 1} = \bar{c}_A^{\beta_A}/(c_A\gamma_A)^{\beta_A}\,(\bar{c}_{0A}/\beta_A - \bar{c}_A/\beta_A - \bar{c}_B/\beta_B), \qquad (34)$$

which can be treated as a generalisation of the Langmuir equation for delocalised adsorption of molecules of different size, reducing to the Langmuir equation when the mixture being sorbed consists of molecules of equal size with $\beta_A = \beta_B = 1$ and $\gamma_A = 1$.

Since in binary adsorption $\bar{\gamma}_i = f(\bar{c}_i, \bar{c}_j)$, the calculation of $\bar{\gamma}_i$ from experimental data is carried out most simply along the $\bar{\theta}_R$ = const. sections. Equations obtained as described above for any value of $\bar{\theta}_R$ = const. are given in Ref.8. In that work[8] all the calculations were carried out from the $\ln K' = f(\bar{\theta}_A)_{\bar{\theta}_R = \text{const}}$ relationship and from the adsorption isotherms of the individual components. We note that the $\bar{K}$ values [which are independent of $\bar{\theta}_R$ under the chosen

standard conditions (6)] can be calculated only from the individual sorption isotherms, since according to (15) and (16) we have

$$\bar{K} = (\bar{K}_A/\bar{K}_B)^{1/\beta_A} \quad (35)$$

or in principle they can be calculated by any analogous method[20].

Since the parameter β (unlike β_A) is practically independent of temperature[18] the temperature dependence of $\bar{K}$ or K can be used to obtain full thermodynamic information on the sorption systems of interest by applying the conventional equations of chemical thermodynamics.

IV. THE OSMOTIC THEORY OF ADSORPTION

1. Adsorption of Pure Substances

By using the concept of an osmotic equilibrium[15-17] we can easily obtain a general isotherm for individual adsorption. This involves inserting into (21) the expression for σ from (20):

$$\bar{K}_A = \bar{c}_A\bar{\gamma}_A/c_A\gamma_A(\bar{c}_{A,max} - \bar{c}_A)\,\bar{\gamma}_*. \quad (36)$$

By comparing this equation with (23) we note that (36) is a special case of (23) for $\beta_A = 1$. This is a direct consequence of the greater generality of the sorption solution model used in the STA.

Using (24) to eliminate $\bar{\gamma}_A$ (with $\beta_A = 1$) we can rewrite Eqn.(36) as[17]

$$c_A\gamma_A = \frac{\bar{\theta}_A}{\bar{K}_A(1-\bar{\theta}_A)}\exp\left[-\frac{\ln\bar{\gamma}_*}{\bar{\theta}_A} - \int_0^{\bar{\theta}_A}\frac{\ln\bar{\gamma}_*}{\bar{\theta}_A^2}\,d\bar{\theta}_A\right], \quad (37)$$

which is identical to the corresponding Eqn.(25) of the STA if $\bar{\gamma}_*$ is replaced by $\bar{\gamma}_A$ in Eqn.(37) and allowance is made for the fact that $\bar{\gamma}_A$ is referred to different concentration scales in Eqns.(25) and (37) [see Eqn.(6)].

We shall examine three special cases.

1. For ideal adsorption $\bar{\gamma}_* = 1$, and Eqn.(37) reduces to the Langmuir equation ($\gamma_A = 1$).

2. If the vacancy solution is regular, we can write from the theory of regular solutions $\ln\bar{\gamma}_* = \bar{\alpha}\bar{\theta}_A^2$ (where α is a constant), and (37) simplifies to the Fowler-Guggenheim equation

$$c_A\gamma_A = \frac{\bar{\theta}_A}{\bar{K}_A(1-\bar{\theta}_A)}\exp[-2\alpha\bar{\theta}_A]. \quad (38)$$

3. The most widely used equation is derived from (37) as described above by using Eqn.(29) (since $s_A = s_*$, it follows that $g_* = g_A$):[15,16]

$$c_A\gamma_A = \bar{c}_A^{g_*}/\bar{K}_A(\bar{c}_{i,max} - \bar{c}_A)^{g_*}, \quad (39)$$

This equation was first obtained in the OTA[15,16] by a strict thermodynamic argument. For adsorption from an ideal gas phase Eqn.(39) can be recast as

$$\ln P_A = \ln P_{A(\bar{\theta}_A=0,5)} + g_A\ln\frac{\bar{\theta}_A}{(1-\bar{\theta}_A)}, \quad (40)$$

which allows the parameters to be determined from the experimental isotherm[15,16]. As was pointed out above, Eqns.(30), (39), and (40) accurately describe the individual adsorption isotherms of many substances on microporous sorbents.

An important and interesting application of the OTA of a single substance was the successful development of a thermodynamic theory of the change in size of microporous adsorbents resulting from sorption[14,23-25]. Correctly denying the thermodynamic validity of Bangham's theory, based on the assumption that $\bar{\phi}_R = \text{const}$, Bering and coworkers[23-25] obtained some fairly strict expressions predicting both an increase and a decrease in the particle size of adsorbents as a result of adsorption.

2. Adsorption of Mixtures

The application of the OTA to mixtures causes a number of difficulties arising from the chosen model of the sorption solution. Thus, in the simplest case of binary sorption the molar volume of a vacancy [see Eqn.(17)] varies as follows with the composition of the sorption solution[17,26,27]:

$$s_*(\bar{z}) = s_A\frac{\bar{c}_A}{\bar{c}_A+\bar{c}_B} + s_B\frac{\bar{c}_B}{\bar{c}_A+\bar{c}_B} = s_A\bar{z}_A + s_B\bar{z}_B. \quad (41)$$

The desired isotherm equation is obtained by solving Eqns.(20) and (21) simultaneously[17]. In this case Eqn.(20) can be combined with (41) to give, for a solution of constant composition $\bar{z}_A$,[27]

$$\sigma W_0 = \frac{W_0}{s_A\bar{z}_A + s_B\bar{z}_B}RT\ln\bar{x}_*\bar{\gamma}_* = \bar{c}_*^0(\bar{z})\,RT\ln[(1-\bar{\theta}_A-\bar{\theta}_B)\,\bar{\gamma}_*], \quad (42)$$

where $\bar{c}_*^0$ is the limiting concentration of vacancies in the sorbent, with a molar volume corresponding to the composition $\bar{z}_A$.

Inserting σ from (42) into (21) yields the adsorption isotherm equation[17], which can be written as

$$\bar{K}_A = \bar{c}_A\bar{\gamma}_A\bar{c}_{0A}/c_A\gamma_A[(1-\bar{\theta}_A-\bar{\theta}_B)\,\bar{\gamma}_*]^{1/\beta_A(\bar{z})}\cdot\bar{c}_*^0(\bar{z}), \quad (43)$$

where $\bar{c}_*^0(\bar{z})$ and $\beta_A(\bar{z})$ depend on the composition ($\bar{z}$) of the sorption solution. Eqn.(43) is formally analogous to the corresponding Eqn.(32) of the STA (allowing for the fact that the $\bar{\gamma}_i$ values are referred to different concentration scales), but it is less convenient than the latter in that it depends on the variables $\beta_A(\bar{z})$ and $\bar{c}_*^0(\bar{z})$, which complicates its practical application even when the $\bar{\gamma}_i = f(\bar{x}_A, \bar{x}_B)$ relationships are known. We note that since $\beta_A(\bar{z})$ and $\beta_B(\bar{z})$ have identical dependences on $\bar{z}$ we can obtain Eqn.(31) by dividing the two equations (43) written for A and B respectively by each other, since $\beta_B(\bar{z})/\beta_A(\bar{z}) = \beta = \text{const}$.

General methods of finding the activity coefficients of the components of the sorption solution are not discussed in the OTA papers, but they are exactly analogous to the methods described above for the STA. The application of the OTA to the general case of adsorption from a multi-component mixture could be greatly simplified by abandoning the conditions $s_* = s_A$, $s_* = s_B$ for one-component adsorption and by assuming (as in the STA) that $s_* = \text{const} \neq s_A \neq s_B$. In particular, Eqn.(43) would correspond exactly to Eqn.(32).

V. ADSORPTION AND THE ENERGY NON-UNIFORMITY OF THE SORPTION CENTRES OF THE SORBENT

In the previous sections we have discussed adsorption equilibria in general, using the activity method to allow (in terms of the activity coefficients of the components of the sorption solution) for molecular interactions and for the energy non-uniformity of the sorption centres of the sorbent. It would be very useful, however, to have a sorption isotherm equation free from the constraints of the activity method. One variant of this approach, proposed by Zel'dovich[28] in 1935, has been examined intensively in recent years (see, for example, Refs.29–39). The basic concept is to set up a general isotherm for the adsorption of one substance

[$\theta(P)$] from local adsorption isotherms applying to energetically uniform sorption centres [$\phi(P, \varepsilon)$] together with a distribution function of the adsorption centres in free energy of adsorption [$\chi(\varepsilon)$]. In the case of a discrete distribution[29,30] we can write

$$\bar{\theta}(P) = \sum_i f_i \varphi_i(P, \varepsilon_i), \tag{44}$$

where f_i is the fractional number of centres having an energy ε_i.

If the function $\chi(\varepsilon)$ is assumed to be continuous we replace (44) by the equation[28-32]

$$\bar{\theta}(P) = \int_0^\infty \varphi(P, \varepsilon)\chi(\varepsilon)\,d\varepsilon. \tag{45}$$

Lastly, for the adsorption of a mixture of i components we have[33-35,38,39]

$$\sum_{i=1}^{i} \bar{\theta}_i(P_n) = \int_{\Delta(n)} \sum_{i=1}^{i} \varphi_i(P_n, \varepsilon)\chi(\varepsilon)\,d\varepsilon, \tag{46}$$

where $n = 1, 2, 3, \ldots, i$, integration is carried out in i-dimensional space, $\sum_{i=1}^{i}$ denotes the total and the local isotherm for the adsorption of the i components of the mixture, and $\bar{\theta}_i$ and ϕ_i are the total and the local adsorption isotherm of the i-th component.

Unfortunately, the solution of the problem in a general form meets a number of fundamental difficulties[29,34]. Since only the total isotherm [$\bar{\theta}(P)$] is available to the investigator Eqns.(44) and (45) do not offer a unique solution of the problem, because a given $\bar{\theta}(P)$ relationship can be obtained by combining $\phi(P, \varepsilon)$ functions of different types, and hence by combining different $\chi(\varepsilon)$ distribution functions. For example, a given $\bar{\theta}(P)$ isotherm can be interpreted as the the sum of a number of Langmuir isotherms for a non-uniform surface, or as an adsorption isotherm for substantial intermolecular interactions on a practically uniform surface. The distribution function $\chi(\varepsilon)$ characterises the adsorbate–adsorbent system rather than the adsorbent. Therefore Eqn.(45) cannot be used to calculate the adsorption isotherms of several adsorbates from the $\chi(\varepsilon)$ function obtained for any one adsorbate. The general solution of (46) is extremely complex[34], and therefore the problem is often simplified by considering the case of a constant difference between the free energies of the adsorbates on the different types of adsorption centre ($\varepsilon_i - \varepsilon_j = \text{const}$).[30,33,34]

Because of these difficulties the approach is usually confined to systems in which the adsorption is obviously localised and the local isotherm can be described with reasonable accuracy by the ideal Langmuir equation. In this case the form of the $\chi(\varepsilon)$ function can be established with great confidence, and the method can be used to solve various problems[35-37]. For example, an interesting application was the derivation of a general equation for the localised adsorption of a mixture on a non-uniform surface and its use in a formal kinetic analysis of heterogeneous catalytic reactions[37,39].

Nevertheless, the wide application of this approach in the description and calculation of sorption equilibria and in the determination of $\chi(\varepsilon)$ functions still presents many problems, and requires substantial further developments.

VI. CALCULATION OF THE EQUILIBRIUM SORPTION CHARACTERISTICS FROM THE MINIMUM AMOUNT OF EXPERIMENTAL INFORMATION

In addition to the strict thermodynamic analysis of adsorption equilibria, another important function of the theory is to develop methods of calculating sorption equilibria for many different systems from the smallest possible volume of experimental information. As we have already pointed out the problem could be solved, in principle, by the methods of molecular–statistical thermodynamics, but unfortunately the difficulties are such as to limit the practical application of these methods to the simplest systems for the time being. Therefore the practical solution of problems usually involves additional, non-thermodynamic relationships derived from experimental data or from very simple (and therefore approximate) physical models of the system of interest. The most successful applications of this approach have been in adsorption from a one-component gas or vapour phase.

1. Calculation of Individual Adsorption Isotherms

The most important advances in the description of isotherms for the individual adsorption of vapours on microporous sorbents were achieved by the theory of volume filling of micropores (TVFM), developed by Dubinin and his coworkers[40-42]. This theory is founded on the temperature-independence of the characteristic free energy of adsorption (E): a thermodynamic analysis shows that this condition can obtain only if the entropy of adsorption is negative, and this restricts the region of validity of the theory to coverages $\bar{\theta}_i > 0.1$.[42]

Within these limitations the equations of the TVFM, applied to monodisperse microporous sorbents and ignoring the non-ideality of the vapour phase, have the form[42-44]

$$\lg \bar{c}_i = \lg \bar{c}_{0i} - \frac{BT^n}{\beta_{i(\mathrm{af})}^n}[\lg(P_{is}/P_i)]^n, \tag{47}$$

where

$$B = (2.303R/E_0)^n; \quad \bar{c}_{0i} = W_0/\bar{v}_{0i} = \bar{c}_{0i}^0 \exp[-\alpha_i(T - T_0)] \tag{48}$$

($\bar{c}_{0i}^0$ is the limiting adsorption at $T = T_0$).

If the adsorbent has a wide distribution of pore radii (carbon sorbents) or of adsorption energies (zeolites used for small adsorbate molecules) an approximate solution is obtained by aggregating two structures with different values of the parameters n and E_0 [40-42] (corresponding to the subscripts 1 and 2):

$$\bar{c}_i = \bar{c}_{0i(1)} \exp\left[-\frac{RT \ln P_{is}/P_i}{\beta_{i(\mathrm{af})}E_{01}}\right]^{n_1} + \bar{c}_{0i(2)} \exp\left[-\frac{RT \ln P_{is}/P_i}{\beta_{i(\mathrm{af})}E_{02}}\right]^{n_2}. \tag{49}$$

For normal micropores of different size $n_1 = n_2 = 2$; for a combination of normal and super-micropores $n_1 = 2$, $n_2 = 3$; for the sorption of small molecules on type A and X zeolites $n_1 = 2$ and $n_2 = 3$ or 4.[41] The n values in (47) undergo similar changes.

Since

$$\beta_{i(\mathrm{af})} = E_i/E_0, \tag{50}$$

where E_0 is the characteristic free energy for vapour adsorption taken as a standard ($\beta_{0(\mathrm{af})} = 1$), it follows that the adsorption isotherms of a substance for various temperatures (lower than T_{cr}) can be calculated by the TVFM from the isotherm measured at a single temperature: hence the thermodynamic adsorption functions and the adsorption isotherms of other adsorbates at different temperatures can also be calculated if $\beta_{i(\mathrm{af})}$ is determined by Eqn.(50).

For calculations of the highest precision $\beta_{i(\mathrm{af})}$ should be obtained from experimental data. For this we need one point on the isotherm of the i-th adsorbate. In a somewhat **rougher** approximation the $\beta_{i(\mathrm{af})}$ values for microporous carbons **can** be expressed as the ratio of the parachors of the i-th and the standard adsorbate[43].

Since Eqns.(47) and (30) describe the same experimental data[44], the TVFM can be regarded as a special case of the STA, applicable to systems in which the $\overline{\gamma}_i = f(\overline{c}_i)$ relationships are described by Eqns.(29) with $g_i = g_R = \text{const}$. Under these conditions $\beta_{i(af)}$ allows for the difference not only in the size of the adsorbate molecules but also in the energy of their interaction with the adsorbent [through Eqn.(50)]. Hence[22]

$$1/\beta_{i(af)} = \beta_i \beta_{en} / \beta_j, \qquad (51)$$

where β_j is the stoichiometric coefficient for the standard substance, and the coefficient β_{en} characterises the difference in interaction energy between the two adsorbates and is close to unity for the sorption of substances of the same type. In this case the $\beta_{i(af)}$ values can be calculated by Eqn.(28), as confirmed by existing experimental data. We note that in systems of this type the $\overline{\gamma}_R = f(\overline{c}_R)$ relationship is the same for all adsorbates.

Dubinin and coworkers[40-42] have discussed in detail the methods of finding the parameters of Eqns.(47) and (49), and have given several examples illustrating the wide applications of the TVFM to the calculation of individual adsorption isotherms and of the corresponding thermodynamic functions. More recently[45] the possibility of extrapolating the results by 50–60 K (to the region of $T > T_{cr}$) was demonstrated.

We must stress that the TVFM offers important information on the structure of the micropores (W_0) and on the adsorption energy (E_0) for microporous adsorbents of different types. This is shown most clearly in studies of adsorption on zeolites, when an independent determination of W_0 by X-ray methods is possible.

The ability of the TVFM to describe experimental data has been improved[46,47] by using n as a variable parameter in Eqns.(47) and (49), but Dubinin showed that this approach is unsatisfactory[48,49]. In the case of carbons the agreement between experimental and calculated isotherms is worse for n values other than $n = 2$: the values of W_0 and E_0 are no longer constant, and the calculated differential heats of adsorption are very different from those measured calorimetrically.

Industrial carbon adsorbents can have a polydisperse micropore structure. Stoeckli[50] tried to apply Eqn.(47) to sorbents of this type, assuming a normal gaussian distribution to describe the distribution of micropore volumes with respect to the parameter B of Eqn.(47). However, experimental data for the sorption of nitrogen, xenon, benzene, and n-butane at different temperatures on E-02 active carbon[50] were shown[48] to be described with equal precision by the Stoeckli equation and by Eqn.(49) with $n_1 = n_2 = 2$, and therefore the two-term equation (49) of the TVFM is a fully acceptable approximation.

Several workers have pointed out that the fundamental postulates of the TVFM are also satisfied (to different extents) for equilibria in other adsorption systems. Thus, Eqn.(47) with $n = 2$ was shown[51-54] to be applicable to adsorption on carbons from aqueous solutions of sparingly soluble organic compounds if P_{is}/P_i is replaced by $\tilde{c}_{is}/\tilde{c}_i$ (where $\tilde{c}_{is}$ is the solubility at the given temperature). A method of determining the micropore volume from adsorption data for systems of this type was developed on this basis[52].

Gur'yanov and coworkers[55,56] have shown that Eqn.(47) can be used to describe multimolecular adsorption and to determine the monolayer capacity. With swelling (polymeric) sorbents Eqn.(47) again gives a satisfactory description of the adsorption isotherms, but the parameter n decreases[57,58] as the degree of crystallinity of the polymer decreases from 0.7 to 0.5 (and even to 0.33), and the temperature-independence of the characteristic free energy is retained in the temperature ranges where the structure of the polymeric sorbent remains substantially constant[58]. These results indicate that the basic postulates of the theory of volume filling are more generally applicable than the variant adopted in the classical TVFM, though further experimental and theoretical work is needed to explain in detail and to justify such a generalisation of the theory.

In the STA and the OTA, which do not stipulate a temperature-invariant characteristic energy of adsorption, thermal adsorption equations can be obtained, in principle, for any temperature range, and in particular for $T \gg T_{cr}$, where the equations of the TVFM are not applicable. This problem was analysed in detail in the original papers on the OTA, and the special forms (39) and (40) of the general OTA equation were shown to describe with good precision the adsorption isotherms for microporous sorbents[15-17]. We should point out that the possibility of determining $c_{i,max}$ by Eqn.(22) was realised relatively recently[17]. In the earlier papers from the same laboratory[49,59-61] the quantity $\overline{c}_{i,max}$ was determined as an empirical parameter ($\overline{c}_{i,emp}$) from the experimental adsorption isotherm plotted as $\ln P_i$ against $\overline{c}_i$, which according to Eqn.(40) has an inflection at the point $(\ln P_{i(\overline{\theta}_i = 0.5)}, \overline{c}_{i,emp}/2)$. The temperature independence of $\overline{c}_{i,emp}$, first established experimentally[60], was later proved by a strict thermodynamic argument. Therefore the thermal equation of the OTA is easily obtained from Eqn.(40), since $\ln P_{i(\overline{\theta}_i = 0.5)}$ is the thermodynamic equilibrium constant of the adsorption, and the function $g(T)$ should be the same as in $\ln \overline{\gamma}_*$:[59]

$$\ln P_i \gamma_i = a + a' \ln\left(\frac{\overline{c}_i}{\overline{c}_{i,emp} - \overline{c}_i}\right) - \left[b + b' \ln\left(\frac{\overline{c}_i}{\overline{c}_{i,emp} - \overline{c}_i}\right)\right] T^{-1}. \qquad (52)$$

When $\overline{c}_i = \text{const}$ Eqn.(52) gives the adsorption isostere equation:

$$\ln P_i \gamma_i = \bar{a} - \bar{b} T^{-1}. \qquad (53)$$

The determination of the five parameters of Eqn.(52) (a, a', b, b', $\overline{c}_{i,emp}$) is discussed in Refs.49 and 59. We know[59-61] that the replacement of $\ln P_i \gamma_i$ by $\ln P_i$ in Eqns.(52) and (53) extends the application of (53) to a large number of systems over a wide temperature range, in spite of the temperature dependence of the enthalpy of adsorption. This fact justifies calculation of the effect of temperature on adsorption over wide temperature ranges, as was demonstrated[59-61] for the adsorption of Ar and Xe on NaX zeolite at $150 \text{ K} \leq T \leq 600 \text{ K}$. Eqn.(52) can describe, in principle, systems in which the heat of adsorption decreases or increases with coverage, though the latter case is not covered by the equations of the TVFM.

Thus the thermal equations of the TVFM and of the OTA are mutually complementary, and depending on the specific features of the practical problem the effect of temperature on the sorption can be calculated by one of the equations given above. We note that the adsorption isotherms of several adsorbates can be calculated, in principle, from the adsorption isotherm of one substance within the framework of the STA. Appropriate methods of realising this possibility are currently being developed.

2. Calculation of the Equilibrium Characteristics of the Adsorption of Binary Mixtures

Studies of the calculation of adsorption equilibria in multicomponent mixtures have been confined almost entirely to binary systems. Many papers have dealt with the possibility

of calculating the isotherm for adsorption from a binary mixture, i.e.

$$\bar{c}_i = f(c_1, c_2) \tag{54}$$

from the experimental isotherms for the adsorption of the individual components

$$\bar{c}_1 = f_1(c_1), \quad \bar{c}_2 = f_2(c_2). \tag{55}$$

Progress in this direction has been discussed in recent review articles[62-64], and we shall not dwell on that work: we shall only mention that in the final analysis a solution of the problem (54), (55) can be found only for ideal sorption solutions or for solutions in which $\Delta U_{i-j} = 0$.[19] In the general case we need additional information on the adsorption of the binary mixture itself. One variant of this approach was recently examined in the OTA for the special case of $g = \text{const}$ when $z = \text{const}$[17,26,27]. The present writer favours a solution of the problem on the basis of experimental information on the sorption of one, two, or three standard mixtures on the given sorbent, i.e. calculation by Eqn.(31) of the values

$$K = f(\bar{c}_A, \bar{c}_B) \tag{56}$$

for a large number of different mixtures of adsorbates from the experimental relationships [Eqn.(56)] for one–three systems and from some properties of the adsorbates (molar volume, dipole moment, polarisability, etc.). Work in this direction is only just beginning, and is limited so far to the accumulation of experimental information and its analysis[6,8,11,12,20,65-68], but the results to date suggest that a solution of the problem (56) will be found.

We should mention two results obtained by the STA which should greatly decrease the need for exploratory experimental work. The first concerns the comparative evaluation of data on the adsorption of binary mixtures from the vapour phase and from the liquid phase on microporous sorbents[20,69].

As we have shown[20], under the standard conditions (6) the thermodynamic constants ($\bar{K}$) and the equilibrium coefficients (K) for sorption from the vapour and the liquid phase are related by the expressions

$$\bar{K}_{\text{vap}} = \bar{K}_{(\text{liq})} \frac{\tilde{c}_{0A} (c_{Bs}\gamma_{Bs})^{\beta}}{\tilde{c}_{0B} (c_{As}\gamma_{As})} = \bar{K}_{\text{liq}} \frac{K^{\beta}_{B,\text{evap}}}{K_{A,\text{evap}}}, \tag{57}$$

(where $K_{i,\text{evap}}$ are the equilibrium constants for the evaporation of the pure liquids), and

$$K_{\text{vap}} = K_{\text{liq}} \frac{\tilde{c}_{0A} (c_{Bs}\gamma_{Bs})^{\beta}}{\tilde{c}_{0B} (c_{As}\gamma_{As})} \cdot \frac{\gamma_A \tilde{\gamma}^{\beta}_B}{\tilde{\gamma}_A \gamma^{\beta}_B}, \tag{58}$$

which allow us to calculate $\bar{K}$ and $K = f(\bar{x}_A)$ for sorption from the vapour phase from data for sorption from the liquid phase, and *vice versa*, since γ_i and $\tilde{\gamma}_i$ are usually known or can easily be determined if necessary. We note that calculation by (58) is legitimate, strictly speaking, if $\bar{\theta}_{A+B} = 1$ for sorption from the vapour phase. However, in most cases the $K = f(\bar{x}_A)$ relationships are almost indistinguishable for $\bar{\theta}_{A+B} > 0.8$–0.9,[20,65] and therefore we can use (58) to calculate equilibria in real, practical vapour–adsorbent systems with $\bar{\theta}_{A+B} > 0.8$. From (57) we can easily obtain an equation for reciprocal calculations of the temperature dependence of sorption (for $\bar{\theta}_{A+B} > 0.8$):[20]

$$\Delta H^0_{\text{vap}} = \Delta H^0_{\text{liq}} + \beta \Delta H^0_{\text{B,evap}} - \Delta H^0_{\text{A,evap}}. \tag{59}$$

We can easily show, also, that if the separation coefficients (α) are determined for the equilibrium compositions of the phases we have[69]

$$\alpha_{\text{vap}} = \frac{\bar{c}_A c_B}{c_A \bar{c}_B} = \frac{\tilde{c}_A c_B}{c_A \tilde{c}_B} \cdot \frac{\tilde{c}_A \tilde{c}_B}{\tilde{c}_A \tilde{c}_B} = \alpha^{\text{vap}}_{\text{liq}} \alpha_{\text{liq}}. \tag{60}$$

In Refs.20 and 69 Eqns.(57)–(60) are tested on the sorption of several binary mixtures on active carbon and on zeolites, and satisfactory agreement between calculation and experiment is obtained. Thus these expressions offer a substantial reduction in the amount of experimentation needed to optimise the separation and purification of particular mixtures by sorption methods.

According to the STA [see (31) and (60)] the separation coefficient α, which is very important in practice because it characterises the selectivity of the sorbent towards the given mixture of adsorbates, is related to the equilibrium coefficient K by the expression

$$\alpha = K(c_B/\bar{c}_B)^{1-\beta}. \tag{61}$$

Therefore, when K is independent of $\bar{\theta}_{A+B}$ (as is usually the case for $\bar{\theta}_{A+B} > 0.5$–0.8) the separation coefficient can be increased to a useful extent by varying the concentration of the components in the bulk phase. In this case the α values can be calculated over a wide range of pressure. Furthermore, if one of the components (say, A) is present in trace amounts we find[70,71] that for $c_B/\bar{c}_B = \text{const}$

$$\ln \alpha = a + bm, \tag{62}$$

where m is the number of carbon atoms in the molecules of homologues present as trace components, and a and b are constants determined from experimental data for two homologues.

The validity of Eqns.(61) (and hence of the basic assumptions of the STA) and (62) was tested experimentally in a number of sorption systems[65,70,71]. Their use can substantially lighten the task of optimising empirically the conditions of separation by sorption. Of course, the calculation of adsorption equilibria for binary and for multi-component mixtures is a complex problem, still not fully resolved. However, the need to solve this problem has been highlighted by the increasing penetration of sorption methods of extracting, separating, and purifying mixtures in industrial practice, and research in this direction has been intensified.

VII. CAPILLARY PHENOMENA AND INFORMATION ON THE PORE STRUCTURE OF THE ADSORBENT

As was stated above, the thermodynamic analysis of multimolecular adsorption processes (which include the transition from pure sorption processes with a sorption volume of limited capacity to condensation processes) is still an unsolved problem. Nevertheless, detailed studies of multi-molecular adsorption and capillary condensation in mesopores (15 Å < r < 2000 Å) have been applied to the characterisation of the structure of mesopores. The theory of this phenomenon was originally developed by Deryagin in 1940; in 1967 de Boer and Broekhoff introduced an approximate correction for the effect of the adsorption field of the pore walls on the chemical potential of the sorbate in their derivation of a modified Kelvin equation; Brunauer and coworkers followed a somewhat different approach. A detailed discussion of that work, with comprehensive lists of references, can be found in Refs.72–75.

The Deryagin–Broekhoff–de Boer method has been recently improved by Dubinin and coworkers, who also allowed for the dependence of the surface tension on the mean radius of curvature of the liquid meniscus[74,75], and used a more universal form of the equation for the t-curve (which describes the dependence of the mean-square thickness (t) of the adsorption layer in the mesopores on the equilibrium relative pressure P/P_s [76,77]).

Solution of this problem requires an assumption as to the geometrical shape of the pores. Attempts to identify the geometry of the pores from the type of hysteresis loop in the isotherm produced by capillary condensation gave ambiguous results[72,73], and therefore the concept of equivalent cylindrical pores is adopted in most calculations. The problem is formulated in such a way that identical capillary evaporation isotherms are obtained for the real adsorbent (with a complex pore structure) and the equivalent adsorbent (with cylindrical pores). The equivalent pore radius (r) is usually defined as double the ratio of the normal cross-sectional area of the pore to the perimeter of the pore.

The classical method (method I) of analysing the distribution of cylindrical mesopore radii is based on the Kelvin equation

$$r_c = 2\sigma \bar{V}_{ol}/RT \ln (P_{is}/P_i), \quad (63)$$

where r_c is the radius of curvature of the spherical meniscus of the liquid adsorbate, formed in the area between the adsorption layers on the walls of a mesopore of radius r. The thickness (t) of the layers is assumed to be independent of r, and is expressed through the t-curve equation, based on the Harkins and Jura adsorption isotherm[73,74,76]:

$$\ln (P_{is}/P_i) = Mt^{-2} - \varphi(t) \quad (64)$$

where M is a constant parameter and $\phi(t)$ is a correction which can be either constant or weakly dependent on t. Hence, in this model

$$r = r_c + t. \quad (65)$$

In the Deryagin–Broekhoff–de Boer method (method II) the effect of adsorption on capillary evaporation from cylindrical pores is allowed for by the function

$$F(t_e) = \bar{\mu}_t - \tilde{\mu}_t, \quad (66)$$

the chemical potential of the adsorbate being assumed to be a function of the distance (t_e) of the liquid–vapour interface from the pore wall, with the function $F(t_e)$ defined by the t-curve (64). The surface tension of the adsorbate is assumed to be independent of the radius of curvature of the liquid meniscus.

In the method developed by Dubinin and coworkers[73–75] (method III) an additional allowance is made for the dependence of σ on r_c by using the Tolman equation (which can also be obtained by molecular statistics[74])

$$\sigma/\sigma_0 = (1 - 2\omega/\rho)^{-1}, \quad (67)$$

in which σ_0 is the surface tension of the planar liquid surface and ρ is the average effective radius of curvature of the meniscus in a cylindrical pore:

$$\rho = r - t_e. \quad (68)$$

However, a detailed analysis by Dubinin[76] of the capillary evaporation isotherm has shown that whereas all three methods should give the same value of r and $t_e \to t$ for $P_i/P_{is} \to 1$, there is a large difference between the radii calculated by methods I, II, and III for the pores from which desorption occurs under the stated conditions (up to 100–150% [79]), and also between the corresponding values of t_e and t. Calculations by methods II and III gave consistent results in this case. It was also shown[76] that the lack of agreement of calculations for $P_i/P_{is} \to 1$ is due to inadequate description of the adsorption in mesopores by the t-curve (64), and that in many systems it would be better to use a more rational equation of the Halsey type

$$\ln (P_{is}/P_i) = \bar{M} t^{-m}, \quad (69)$$

where $\bar{M}$ and m are constant parameters. By replacing (64) by (69) the discrepancy between calculations by methods I, II, and III at $P_i/P_{is} \to 1$ could be eliminated[76,77].

The equations of method III in this case become[76,77]

$$\ln (P_{is}/P_i) - \bar{M} t_e^{-m} - \sigma_0 \bar{V}_{ol}/RT (r - t_e - \omega) = 0, \quad (70)$$

$$r - t_e = \frac{2\sigma_0 \bar{V}_{ol} (r - t_e)}{RT (r - t_e - 2\omega) \ln (P_{is}/P_i)} + \frac{2\bar{M}}{(r - t_e) \ln (P_{is}/P_i)} \left[\frac{r^{2-m}}{(1-m)(2-m)} - \frac{r t_e^{1-m}}{(1-m)} + \frac{t_e^{2-m}}{(2-m)} \right]. \quad (71)$$

The calculations, described in detail in Refs.74–79, were taken as far as a minimum pore size of 16–17 Å. In the case of these micro-mesoporous sorbents the specific surface area of mesopores ($\bar{S}$, $m^2\ g^{-1}$) was determined independently by the "t/F method", developed and proposed in Refs.79 and 80. Essentially, the method consists in calculating the sorption in micropores by Eqn.(47), subtracting the adsorption calculated by the TVFM from the total adsorption experimentally observed, and thus arriving at the sorption in mesopores only. With other adsorbents $\bar{S}$ was determined also by the BET method.

The total volumes of mesopores calculated by the three methods are almost indistinguishable, but the mesopore surfaces are given more accurately by methods II and III. However, the basic difference between these three methods is in the distribution of mesopore volumes with respect to radius. The effect arises[74] from differences in the dependence of P_i/P_{is}, t, and t_e on the mesopore radius in the three methods of calculation. Thus, for $r > 150$–200 Å the P_i/P_{is} values do not differ significantly in the three methods, but the t_e values in methods II and III are similar but different from t (method I). This means that the correction for the $\sigma(\rho)$ variation (method III) is significant only for $r < 150$–100 Å. The intermediate mesopore region (radii from 100 to 50 Å) is characterised by large differences between the t_e and P_i/P_{is} values calculated by the three methods, the effects becoming even more marked for $r < 50$ Å. In this range of mesopore radii the $\sigma(\rho)$ dependence makes a substantial contribution to the final result and must obviously be included in the calculation. The correction makes the t_e values given by method III smaller than the other values. On changing from method I to method III the mesopore volume distribution curve shifts towards larger radii. The differences are large, and they give rise to large changes in the porosity characteristics which cannot be ignored, even to a rough approximation.

Thus Dubinin's variant of the calculation of the structural characteristics of mesopores is an important development of the method, though it is only a first step in the required direction and needs to be made more precise, especially in the region of 16 Å $< r <$ 30 Å. Furthermore, allowance for the real structure of the mesopores (flat, cylindrical, spherical) may also result in significant changes of the pore radius distribution function[75]. Therefore the structural characteristics obtained by methods I–III are arbitrary to a greater or lesser extent, and allowance for the real structure of the mesopores has become the most pressing of the theoretical problems.

* * *

This brief review of the present state of the thermodynamic theory of adsorption shows that substantial progress has been made in recent years towards the development of a strict thermodynamic theory of sorption. A full

thermodynamic analysis of various sorption systems is possible by the OTA, and even more so by the STA.

The TVFM, and also the OTA and the STA, have led to successful developments of methods of calculating sorption equilibria for individual adsorption from a single experimental isotherm. Important advances in this direction have been made also for the adsorption of mixtures.

Progress in methods of calculating mesopore structures from capillary condensation phenomena has been substantial.

Nevertheless the increasing application of sorption methods in the chemical industry has created a need for even greater scientific efforts in the study of two-component and multi-component adsorption. In this context the development of methods of calculating adsorption equilibria in multi-component systems from the minimum amount of experimental information becomes a major objective of the theory of adsorption.

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The Paramagnetic Probe Method in Adsorption and Catalysis

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The application of the paramagnetic probe method to studies of heterogeneous systems is discussed. By analysing the ESR spectra of the adsorbed probes (nitroxyl radicals) information is obtained on the interaction of the probe with the surface of silica gel, aluminium oxide, alumina-silicas, etc. Special attention is paid to the formation of donor-acceptor complexes with co-ordinationally unsaturated cations of the surface, and to the mobility of molecules in the adsorption layer. 53 references

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I. INTRODUCTION

The fundamental problems in adsorption and catalysis are the formation of the adsorption layer, the nature and the number of adsorption and catalytically active centres, the type of interaction between these centres and the adsorbed molecules, and the dynamics of the adsorption layer. Significant progress towards the solution of these problems has been made by using spectroscopic methods, and in particular the ESR method. The latter method is widely applied in studies of catalysts containing paramagnetic ions and radiation-induced defects as active centres, and also in studies of the interaction of various molecules with these centres and of the radical and ion-radical states created by the interaction of some adsorbates with the active surface of solids[1,2].

The paramagnetic probe method has been used in recent years to study catalysts and adsorbents which do not contain paramagnetic centres, in particular very commonly used materials such as alumina and some other oxides, alumina–silicas, and zeolites. The method consists in adding to the system paramagnetic particles (probes) and monitoring their ESR spectra, whose changes reflect the properties of the environment which the probes experience. In this review we shall be concerned mainly with the results obtained by using stable nitroxyl radicals as probes. The theory of the ESR spectra of these radicals is adequately developed[3,4], and by analysing the ESR spectra of adsorbed nitroxyl radicals we can study the interaction of these particles with the surface adsorption centres and in many cases we can observe the adsorption centres directly. Equally important is the possibility of measuring the velocity of the rotational and translational motion of the adsorbed molecules, i.e. of studying the dynamics of the adsorption layer.

Nitroxyl radicals offer a convenient model of adsorbates of the donor type. They all contain the $>$N–O· fragment, which includes an unpaired electron as well as having normal donor properties. In addition to the $>$N–O group the radicals may contain other donor groups able to interact specifically with the active centres of the adsorbent. The presence of an unpaired electron allows the behaviour of these molecules in the adsorption layer to be monitored by ESR but does not otherwise affect the adsorption. Therefore studies of adsorption processes by the paramagnetic probe method are qualitatively applicable to a large number of adsorbates widely used in industry.

II. INTERACTION OF NITROXYL RADICALS WITH THE SURFACE OF OXIDE CATALYSTS

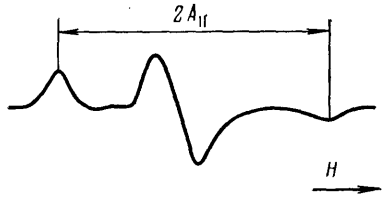
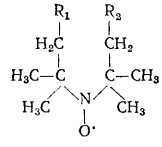
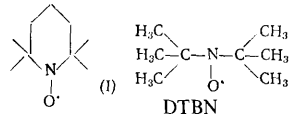


Figure 1. Determination of the anisotropy constant for the hyperfine interaction of an unpaired electron with the ^{14}N nucleus ($A_\parallel$) in the ESR spectra of randomly oriented "frozen" nitroxyl radicals[5].

The ESR spectrum of nitroxyl radicals, which include the fragment



for example, 2,2,6,6-tetramethylpiperidine-1-oxyl (I) or di-t-butylnitroxyl (DTBN)



(I) DTBN

consists of three hyperfine structure (HFS) components due to interaction of the unpaired electron with the ^{14}N nucleus (nuclear spin $I_N = 1$). The anisotropy constant $A_\parallel$ of the hyperfine interaction (HFI) of the unpaired electron with the ^{14}N nucleus (Fig.1) is a function only of the electron spin density on the nitrogen atom. If the $>$N–O· group takes part in any interaction, for example by forming a donor–acceptor or a hydrogen bond, the electron spin density

on the nitrogen atom changes, and $A_{\parallel}$ also changes[4,6]. This effect is illustrated in Table 1. When these interactions are absent or insignificant, as in solutions in non-polar solvents or in pyridine frozen to a glass at 77 K, $A_{\parallel}$ amounts to 34–35 Oe. Hydrogen bond formation raises $A_{\parallel}$ to 38 Oe, and protonation to almost 40 Oe.

Table 1. *A* values (Oe) for the ESR spectra of nitroxyl radicals in different systems.

System	DTBN (Ref.6)	Radical (I) (Ref.7)
Glassy matrix		
n-Hexane	34.1	—
Toluene	34.6	34.6
Pyridine	35.2	35.3
Aqueous glycerol	—	37.8
Phenol	38.3	—
H_3PO_4 (10–40%)	—	39.5
Adsorption on silica gel		
Clean surface	38.6	38.0
Sample immersed in toluene	—	38.0
Adsorbed monolayer of pyridine	—	36.2
Sample immersed in pyridine	35.2	—

The interaction of the radicals (I) and DTBN with SiO_2 and hydroxylated Al_2O_3 surfaces has been found to give a high (38 Oe) value of the constant $A_{\parallel}$, characteristic of the formation of hydrogen bonds with the surface OH groups. The result was not unexpected, since hydrogen bond formation between donor molecules and the surface OH groups had been observed by i.r. spectroscopy[8]. However, the ESR method can be used to monitor changes in the interaction between radicals and surfaces resulting from the adsorption of other substances. This feature is very important because optical spectroscopic methods do not usually give this information.

An excess of non-polar molecules (toluene, CCl_4) does not affect the bond between radical (I) and the OH groups of the surface ($A_{\parallel}$ is unchanged), but donor molecules (for example, pyridine) can displace the radicals from the surface OH groups by being competitively adsorbed, as shown by changes in the $A_{\parallel}$ constant. Thus, when the surface is covered with a monolayer of pyridine the $A_{\parallel}$ value of radical (I) is 36.2 Oe. The displaced radical evidently interacts with polar elements of the surface structure, since the $A_{\parallel}$ constant remains higher than for non-polar solvents. We shall arbitrarily regard the radicals displaced from specific adsorption centres as physisorbed.

Sistovaris and coworkers[9] investigated the interaction of various nitroxyl radicals with a modified silica gel surface by analysing changes in the $A_{\parallel}$ parameter.

However, information on the nature of the adsorption centre can be obtained not only through measurements of $A_{\parallel}$. Complex formation between the >N–O group and Lewis acids with cations having non-zero nuclear spin can give rise to an additional hyperfine structure in the ESR spectra[10–12]. On γ-Al_2O_3 (activation temperature $T_a > 150$ °C) the radical (I) forms a bond with the acceptor centres (coordinationally unsaturated Al^{3+} ions) to give a surface complex with the >N–O→Al< structure[13]. The ESR spectrum of this complex contains components from the interaction of the unpaired electron with the ^{27}Al nucleus ($I_{Al} = 5/2$, Fig. 2*a*). This spectrum is fully analogous to the spectrum of the complex between the radical (I) and $AlCl_3$ in a glassy toluene solution (Fig. 2*b*).

Similar spectra for the complex between radical (I) and the acceptor centres have been observed not only on Al_2O_3 but also on alumina–silicas, fluorinated alumina[11], type HY zeolite[14] (in all of which the complex is formed with the Al^{3+} ion), and on Ga_2O_3 (complex with the Ga^{3+} ion). Thus the radical (I) acts as a selective indicator of centres of this type. This is one of the few instances of direct spectroscopic observation of the adsorption centre itself.

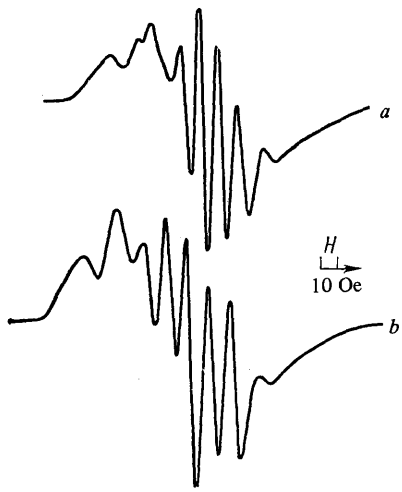


Figure 2. ESR spectra of the nitroxyl radical (I):[11] (*a*) complexed with the coordinationally unsaturated Al^{3+} ions of activated γ-Al_2O_3 at 20 °C; (*b*) complexed with $AlCl_3$ in toluene at −110 °C.

The ESR spectra of the complex with the coordinationally unsaturated Al^{3+} ion have been observed also with DTBN used as the paramagnetic probe[6]. By modelling the experimental spectra on a computer the authors were able to show that the constants of the anisotropic hyperfine interaction with the ^{14}N and ^{27}Al nuclei are somewhat different for different catalysts (Table 2). The differences are ascribed to the difference in strength of the acceptor centres of these catalysts.

Table 2. Anisotropic hyperfine interaction constants (Oe) of an unpaired electron with the ^{14}N and ^{27}Al nuclei in the complex between DTBN and the Al^{3+} ions of various catalyst surfaces[6].

Constant	Al_2O_3	Type HY zeolite	Al_2O_3·SiO_2
$A_{\parallel}^{N}$	42.5	44.6	45.3
$A_{\parallel}^{Al}$	14.6	14.8	16.4
$A_{\perp}^{Al}$	11.2	12.5	14.2

Many workers now consider not only the difference in strength of the acidic centres on different catalysts but also the distribution in strength of the acidic centres (including acceptor centres) on any one catalyst[15]. In this case the

shift of the electron density from the donor (nitroxyl radical) towards the acceptor (Al^{3+} ion) should be different for different centres on the same surface. Therefore the observed ESR spectrum of the complex between the nitroxyl radical and the acceptor centre should be the sum of a number of spectra differing in the value of the constant for the HFI of the unpaired electron with the ^{14}N and ^{27}Al nuclei. In the models[6] of the spectra of the complex between the nitroxyl radical and the Al^{3+} ions on various catalyst surfaces no allowance was made for the distribution of the acceptor centres in acidic strength, i.e. each spectrum was characterised by a single value of the anisotropic HFI constant. By varying these constants the model spectra could be made to reproduce the experimental spectra satisfactorily. These values of the HFI constant are given in Table 2.

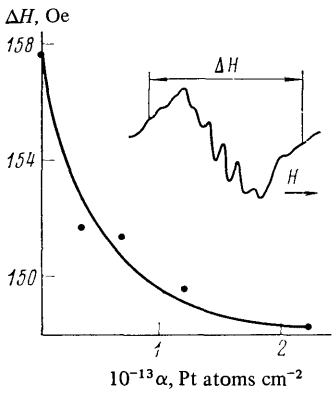


Figure 3. Variation of the parameter $\Delta H = 2A_{\parallel}^{N} + 5A_{\parallel}^{Al}$ for the ESR spectrum of adsorbed radical (I) with the concentration of platinum on a γ-Al_2O_3 surface.

We have recently shown† that the ESR spectra of the radical (I) complexed with coordinationally unsaturated Al^{3+} ions on a γ-Al_2O_3 surface is indeed the sum of a number of spectra for the radical (I) complexed with acceptor centres of different strength. Hence the parameter ΔH (defined[6] as $\Delta H = 2A_{\parallel}^{N} + 5A_{\parallel}^{Al}$) is an average quantity which can be used as a measure of the distribution in strength of the acceptor centres (Fig.3). We note that a change in acceptor strength causes a change in the same sense in both the constants $A_{\parallel}^{N}$ and $A_{\parallel}^{Al}$. We can therefore use the parameter ΔH to describe the effect of various factors (such as the surface activation or modification temperature) on the strength distribution of the acceptor centres.

For example, when platinum is deposited on a γ-Al_2O_3 surface the ΔH parameter decreases (Fig.3), showing that the distribution of acceptor centres has been shifted towards lower strengths (i.e. that the acceptor properties of the surface have been weakened by the metal–substrate interaction). Raising the activation temperature of the γ-Al_2O_3 increases the contribution from strong acceptor centres.

The adsorption of a small amount of the radical (I) on an activated γ-Al_2O_3 surface results in almost total complexing of the radical with the acceptor centres. This observation is consistent with the general belief that Al^{3+} ions are stronger than OH groups as adsorption centres for donor molecules. Similar results were obtained by Lozos and Hoffman[6] for the adsorption of DTBN at room temperature. Somewhat unexpectedly, these workers also observed a reversible migration of the DTBN from the acceptor centres to the OH groups when the temperature was lowered to −78 °C (indicated by the appearance of a triplet spectrum for the complex). Their estimate of the change in enthalpy accompanying the transfer of the radical from an OH group to an acceptor centre is approximately +5 kcal $mole^{-1}$. This result is explained in terms of the formation of a complex[16] between a coordinationally unsaturated Al^{3+} ion and a surface hydroxyl group. This requires the breaking of a bond between the OH group and the Al^{3+} ion in order to form a complex between the radical and the acceptor centre, with a corresponding expenditure of energy. However, an attempt to reproduce Lozos and Hoffman's experiment in our laboratory did not give the same result: no changes were observed in the ESR spectrum of activated alumina samples containing DTBN or the radical (I), even after lengthy storage at −78 °C, the spectrum at all times indicating complex formation with the Al^{3+} ions.

Non-polar adsorbates do not dissociate the complex between radical (I) and the acceptor centres: the characteristic spectrum is unchanged (Fig.2*a*) by the addition of an excess of toluene to the system. Polar adsorbates with donor properties (pyridine, n-butylamine, alcohols, water, ammonia) displace the radical (I) from the acceptor centres as shown by the appearance of a triplet spectrum[13,17,18].

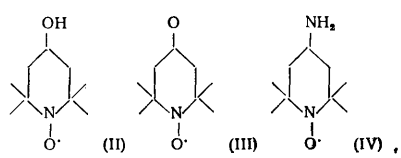
The displacement of the radical (I) from the acceptor centres begins at low coverages of the surface by donor adsorbates (10–30% of a monolayer)[18]. The molecules of (I) detached from the acceptor centres are held on OH groups, as shown by the change of the spectrum of the complex into a triplet spectrum with $A_{\parallel} \cong 38$ Oe.

The surface of fluorinated Al_2O_3 and of alumina–silicas contains acidic centres of two types: protonic and aprotic. The ESR spectrum of radical (I) adsorbed on these surfaces includes a contribution from the complex between the radical and the Al^{3+} ions[11]. Therefore, radical (I) is able to "discover" the acceptor centres irrespective of the protonic acidity of the catalyst. However, the ESR spectrum invariably contains a contribution from a triplet with $A_{\parallel} \cong 40$ Oe.[19] This large value of $A_{\parallel}$, almost identical to the $A_{\parallel}$ value in phosphoric acid (39.5 Oe), suggest complex formation between the >N–O· group of the radical and the protonic centres of the surface. This interpretation of the triplet with $A_{\parallel} = 40$ Oe is consistent with the observation that its contribution to the spectrum of the adsorbed radical (I) decreases when the protonic acidity of fluorinated Al_2O_3 is suppressed by exchange with Na^+ ions.

Thus radical (I) can be used for the qualitative detection of acidic centres of both the protonic and the aprotic (acceptor) type.

Donor pyridine molecules can displace radical (I) from both protonic and aprotic acidic centres, as shown by the decrease in the $A_{\parallel}$ constant of the triplet and the decreased spectral contribution from the complex produced by an increase in the coverage of the alumina–silica surface by pyridine[19].

By varying the structure of the nitroxyl radical we can model interactions of different adsorbates with the surface[7]. Thus, the radicals (II)–(IV) below contain, in addition to the N–O· group, a second donor group (oxy, oxo, and amino respectively):



†T.V.Bychkova, E.V.Lunina, A.K.Selivanovskii, and B.V.Strakhov, Zhur.Fiz.Khim. (in press).

In this case the two donor groups of a given molecule can compete for a specific adsorption centre. The spectrum of the complex between the N–Ȯ group and the Al^{3+} ions is not observed when the radicals (II)–(IV) are adsorbed on an activated Al_2O_3 surface. Hence we may conclude that the >N–Ȯ group is weaker as a donor than the oxy, oxo, or amino group. The parameter $A_\parallel = 36$ Oe suggests interactions between the paramagnetic group and the polar parts of the Al_2O_3 surface. Adsorption of the radicals (II)–(IV) on SiO_2, like their adsorption on Al_2O_3, results in bond formation between the specific adsorption centres (OH groups on the SiO_2 surface) and the second donor group (rather than the >N–Ȯ group), with $A_\parallel = 36.8$ Oe. This value of $A_\parallel$ indicates that the paramagnetic group is interacting with the polar elements of the SiO_2 surface.

Thus, for the "two-centre" molecules (II)–(IV) we must postulate a two-point adsorption model.

An excess of non-polar toluene molecules has no effect on the bond between the >N–Ȯ groups of the radicals (II)–(IV) and the SiO_2 or Al_2O_3 surface (as shown by the invariance of the $A_\parallel$ parameter). Pyridine breaks this bond, lowering $A_\parallel$ to 34.6 Oe at monolayer coverage[7].

The interaction of the nitroxyl radicals with specific adsorption centres can be detected also by observing the rotational mobility of these radicals on the surface[7]. It appears from these measurements that in order to displace from the specific adsorption centres the radicals (II)–(IV), which contain very strongly donating groups, we require higher concentrations of donor adsorbates than in the case of radical (I). Radical (IV) is more difficult to displace from the specific adsorption centres than radical (II): this reflects the more marked electron-donor properties of the amino group as compared to the oxy group.

It is clear from these results that the paramagnetic probe method can be used to monitor the distribution of typical donor molecules (the nitroxyl radicals) among adsorption centres of three types (hydroxyl groups, protonic acidic centres, and aprotic acidic centres), and to observe changes in this distribution caused by the adsorption of various substances.

III. INTERACTION OF DONOR MOLECULES WITH THE ACCEPTOR CENTRES OF γ-Al_2O_3

The displacement of radical (I) from acceptor centres by donor molecules (see above) can be used to investigate the interaction between these donor molecules and the acceptor centres[18]. After the adsorption of small amounts of donor molecules on an Al_2O_3 surface some of the acceptor centres remain free. The radical (I) (in amounts much smaller than the number of acceptor centres) is complexed with these free centres to give the ESR spectrum shown in Fig. 2*a*. If all the acceptor centres are blocked by molecules of the donor adsorbate the radical (I) has to compete with the donor adsorbate for the acceptor centres. Under these conditions some of the molecules of radical (I) are adsorbed on OH groups, and a triplet component appears# in the ESR spectrum of the adsorbed radical (I). Hence, by using the radical (I) as an indicator of free acceptor centres we can determine the amount of different donor molecules (bases) needed to fill the acceptor centres.

#The ESR spectra were recorded after lengthy (~5 days) storage of the sample at room temperature, to allow sufficient time for the redistribution of adsorbates over the adsorption centres to go to completion (see below).

It is clear from Table 3 that different surface concentrations are needed to fill all the acceptor centres of γ-Al_2O_3 with different bases. To account for this difference an independent study of each base is required, but one possible reason is the difference in selectivity of the bases with respect to the adsorption centres of the surface. Thus, pyridine is selectively adsorbed on the acceptor centres[20]. Water molecules can be strongly held by the OH groups, and have a tendency to associate on the surface[21]. The low effectiveness of alcohols in this respect is due, no doubt, to their chemisorption on OH groups with formation of alcoholates[22].

Table 3. Surface concentration of donor molecules (α) needed to fill the acceptor centres of γ-Al_2O_3 ($T_a = 470$ °C).[18]

Base	$10^{-13}\alpha$, cm^{-2}	θ*, % of monolayer
Pyridine	3±0.5	8
n-Butylamine	3±0.5	6
Ammonia	7±1	9
Isopropanol	7±1	20
n-Butanol	8±1	25
t-Butanol	7±1	22
Water	16±2	17

*θ is the degree of coverage of the surface.

The most interesting of the adsorbates which were examined is water, since it is a component of practically all catalytic systems, and the amount and form of the adsorbed water can have a profound effect on the activity of acidic heterogeneous catalysts. The number of water molecules needed to cover all the acceptor centres of γ-Al_2O_3 is $(16 \pm 2) \times 10^{13}$ cm^{-2} (see Table 3). This amount is independent of the adsorption temperature between 20 and 250 °C.[23] However, water adsorbed at 20 °C is removed from the surface much more easily than water which has been adsorbed at higher temperatures. Thus, in samples treated[23] with saturated water vapour at 20 °C for 2 days and then activated at 300 °C for 4 h in a vacuum of 10^{-5} Torr the concentration of acceptor centres§ was 2.0×10^{13} cm^{-2}. The acceptor properties of samples re-hydroxylated at a higher temperature (300 °C, 2 h, in an atmosphere of water vapour) and then activated under the same conditions (300 °C, 10^{-5} Torr, 4 h) were much less marked (0.8×10^{13} cm^{-2}).§ Evidently, the form of the adsorbed water varies with the adsorption temperature: molecular adsorption is predominant at low temperatures, and at higher temperatures the adsorption is mainly dissociative, with formation of OH groups, as indicated also by i.r. spectroscopic studies[24].

Ammonia is one of the probes most widely used in i.r. spectroscopy to analyse the acidic properties of the surface of oxide catalysts[8]. The amount of ammonia chemisorbed is taken as a measure of the concentration of acidic centres on the catalyst (in particular the aprotic centres of γ-Al_2O_3 [25]). However, the validity of this assumption requires justification: ammonia is known, from studies by i.r. spectroscopy[24], to interact not only with electron-acceptor centres (aprotic acids) but also with the surface oxygen ions of γ-Al_2O_3.

§The concentration of acceptor centres was determined by titration with pyridine, using the radical (I) as indicator[20].

The low selectivity of the adsorption of ammonia on the acceptor centres of γ-Al_2O_3 has been demonstrated also by the paramagnetic probe method[53]. 2.5×10^{13} cm^{-2} of pyridine was adsorbed on a γ-Al_2O_3 surface containing 3×10^{13} cm^{-2} of acceptor centres. 4.5×10^{13} cm^{-2} of ammonia was needed to fill the 0.5×10^{13} cm^{-2} acceptor centres which were still free. Hence, at least 4×10^{13} cm^{-2} of ammonia can be adsorbed on other centres.

We note that this amount (4×10^{13} cm^{-2}) does not change when the activation temperature of the γ-Al_2O_3 is raised to 700 °C, or when the catalyst is treated with hydrogen at high temperatures. A large volume of indirect information, as well as the results obtained by i.r. spectroscopy[24], suggests that in addition to the acceptor centres and oxygen ions on the surface of γ-Al_2O_3 can act as adsorption centres for ammonia.

IV. USE OF NITRIC OXIDE AS A PARAMAGNETIC PROBE

Many workers have used nitric oxide (NO) as a paramagnetic probe. Like the nitroxyl radicals, NO is an indicator of free acceptor centres on a catalyst. When adsorbed on these centres NO gives an ESR spectrum containing hyperfine structure from one ^{27}Al nucleus (Fig. 4*a*). However, in contrast to the radical (I), the ESR spectrum of NO can be observed only if the probe molecule is exposed to a fairly high electrostatic field gradient[27]. The NO molecules which are adsorbed on centres lacking in high crystal field gradient do not contribute to the ESR spectrum. This feature, together with the possibility of dimerisation of NO, is responsible for the low intensity of the ESR spectra of adsorbed nitric oxide, apparently uncorrelated with the number of adsorbed molecules[27-29] (unlike the ESR spectra of nitroxyl radicals). Another special feature of NO as a paramagnetic probe is that the NO molecules at room temperature are only weakly adsorbed on surfaces such as Al_2O_3, alumina–silicas, and zeolites. Substantial adsorption occurs only when the temperature is lowered to 77 K.

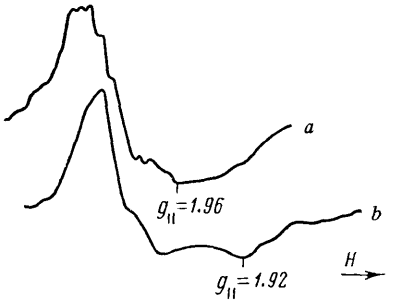


Figure 4. ESR spectra of nitric oxide adsorbed on γ-Al_2O_3 at −196 °C:[29] (*a*) adsorption on an activated γ-Al_2O_3 surface; (*b*) adsorption on a γ-Al_2O_3 surface containing 5×10^{13} cm^{-2} pyridine molecules.

This latter factor is extremely important, since in the quantitative determination of aprotic acidity by titration with bases (or in studies of the filling of acceptor centres) using nitroxyl radicals as indicators competition for the acceptor centre can occur between the titrant base (for example, pyridine) and the nitroxyl radical. This competition can distort the result of the determination. When NO is used as a probe its adsorption takes place at such low temperatures that the other adsorbed molecules are practically immobile. Therefore the competition is kinetically excluded (though it may be allowed thermodynamically). The concentrations of acceptor centres on γ-Al_2O_3 measured by pyridine titration using the radical (I) and NO as indicators [$(3.0 \pm 0.5) \times 10^{13}$ and $(4.0 \pm 0.5) \times 10^{13}$ cm^{-2} respectively] are in acceptable agreement[29]. This means that the competition between the base and the indicator does not play a major role when the number of acceptor centres is measured by the adsorption of pyridine using radical (I) as the indicator.

By using NO as the paramagnetic probe it was shown that 2,6-dimethylpyridine, like pyridine, is selectively adsorbed on the acceptor centres of a γ-Al_2O_3 surface. However, the presence of two methyl substituents makes the bond between the 2,6-dimethylpyridine molecules and the acceptor centres much weaker than in the adsorption of pyridine (steric hindrance).

When NO is adsorbed on a γ-Al_2O_3 surface two types of centre can be distinguished in the ESR spectra[26,29]. The first type are the centres containing coordinationally unsaturated Al^{3+} ions: they give an ESR spectrum with HFS from the Al nucleus. Centres of the second type also have a large crystal field gradient, but their ESR spectrum does not contain HFS from the Al nucleus (Fig. 4*b*).

It is interesting to note that in the adsorption of pyridine the centres of the first type are filled first[29]. As long as the concentration of pyridine does not exceed 3×10^{-13} cm^{-2}, centres of the first type remain free on the Al_2O_3 surface. NO is adsorbed on these centre giving the ESR spectrum shown in Fig. 4*a*. A pyridine concentration of 4×10^{13} cm^{-2} is sufficient to block all the centres of the first type. In this case the NO is adsorbed on centres of the second type, and gives the ESR spectrum shown in Fig. 4*b*. Thus, in the first instance both pyridine and NO are adsorbed on centres of the first type, leaving the second type of centre free. A similar behaviour is observed with 2,6-dimethylpyridine.

When ammonia is adsorbed, centres of the first type are observed in the ESR spectra of NO until the concentration of ammonia reaches 8×10^{13} cm^{-2}. At still higher concentrations of ammonia the ESR spectrum of NO cannot be detected. Hence, the ammonia molecules (unlike pyridine) can fill centres of both types, the probability of filling centres of the second type being equal to (or greater than) the probability of filling centres of the first type (coordinationally unsaturated Al^{3+} ions).

V. DETERMINATION OF THE CONCENTRATION OF ACCEPTOR CENTRES IN γ-Al_2O_3

When a small amount of the nitroxyl radical (I) is adsorbed on an activated γ-Al_2O_3 surface all the adsorbed molecules are bound to surface acceptor centres (only the spectrum shown in Fig. 2*a* is observed[30]). Hence, this radical is selectively adsorbed on the acceptor centres. Assuming that the OH groups are much weaker adsorption centres than the acceptor centres we can expect the acceptor centres to be filled first, followed by the OH groups, as the concentration of the radical on the surface is increased. This idealised behaviour is illustrated by the broken lines in Fig. 5. The experimental curves (full lines) are not very different, though they show a marked smoothing of the sharp breaks (Fig. 5). Since the surface complex consists of one molecule of radical (I) and one acceptor centre the number of acceptor centres in the sample can be identified with the maximum amount of radical (I) bound in the complex.

The high sensitivity of ESR allows small concentrations of acceptor centres to be determined (as in γ-Al_2O_3 samples activated at low temperatures). For example, on γ-Al_2O_3 activated in a vacuum at 150 °C a concentration of ~10^{11} cm^{-2} has been observed[30]. When the vacuum heat treatment temperature was raised to 200 °C the concentration of acceptor centres rose to 4×10^{12} cm^{-2}.[30]

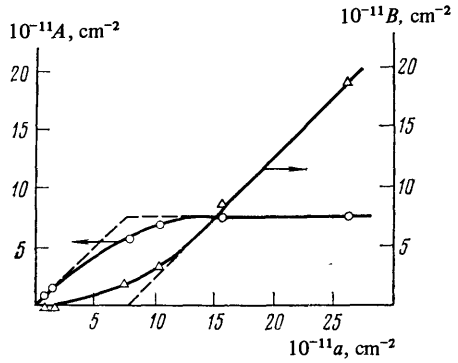


Figure 5. Dependence of the concentration of radical (I) complexed with Al^{3+} ions (*A*) and of the concentration of radical (I) not complexes with Al^{3+} ions (*B*) on the total concentration of radical (I) adsorbed on a γ-Al_2O_3 surface (*a*) activated in air at 300 °C.[30] The broken lines show the idealised dependence.

As the vacuum activation temperature is further increased the concentration of acceptor centres increases still further. The determination of these large concentrations requires the addition of large amounts of radicals. This introduces a difficulty, inherent in ESR: the dipole–dipole interaction causes broadening of the HFS of the spectrum when the radicals are closely spaced on the surface, and the spectrum is converted into a broad, structureless line. In such a spectrum it is very difficult to resolve the contribution from the spectrum of Fig. 2*a*, i.e. to determine the amount of radical (I) bound in the complex, and hence the number of acceptor centres[30]. In this case another approach can be followed: titration of the acceptor centres with an organic base (pyridine) using radical (I) as the indicator[20]. The choice of pyridine is dictated by the outstanding effectiveness of this molecule in filling the acceptor centres (see Table 3). The surface concentration of pyridine for which the filling of the acceptor centres is complete is taken as a measure of the concentration of acceptor centres. The acceptor properties of γ-Al_2O_3 activated at widely different temperatures were determined by this method: the results are summarised in Fig. 6.

However, the titration method is, to some extent, indeterminate, since the titrant base can be adsorbed also on adsorption centres other than the acceptors. The validity of the results can be estimated by analysing a similar series of samples by an independent method[20]: from the concentration of the paramagnetic donor–acceptor complex formed by anthraquinone[31]. The results are shown in Fig. 6, together with the concentrations of acceptor centres in γ-Al_2O_3 samples activated at low temperatures[31]. These values were obtained by a direct method, i.e. as the maximum concentrations of the complexed form of radical (I) (see above). As Fig. 6 shows, the agreement between the three independent methods is good. We may therefore suggest that all the acceptor centres detected by these methods are the same: coordinationally unsaturated Al^{3+} ions. In this sense the work is very different from previous publications[15,32], in which the numerical results were highly tentative.

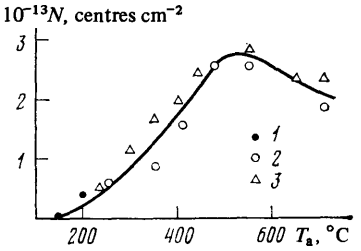


Figure 6. Dependence of the concentration of acceptor centres on γ-Al_2O_3 on the activation temperature of the catalyst[20]. Concentrations determined: *1*) as the limiting concentration of complexed radical, *2*) by titration with pyridine using the radical (I) as indicator, *3*) from the concentration of the paramagnetic donor–acceptor complex with anthraquinone.

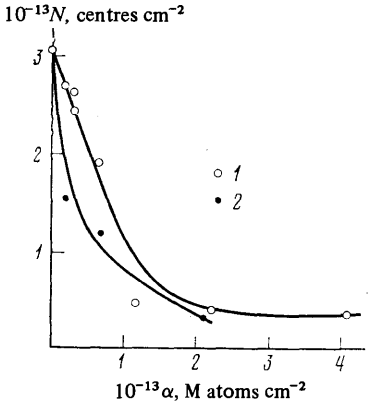


Figure 7. Concentration of acceptor centres on the surface of alumina–platinum and alumina–palladium catalysts against concentration of metal M: *1*) platinum, *2*) palladium.

Pyridine titration with radical (I) as indicator was used to measure the concentration of acceptor centres on alumina–platinum and alumina–palladium catalysts¶. We see from the results (Fig. 7) that the introduction of the metal lowers the concentration of acceptor centres very significantly, especially in the range $0.2–1.0 \times 10^{13}$ metal atoms cm^{-2}. The decrease in the concentration of acceptor centres is due to the interaction of the deposited metals with the γ-Al_2O_3 surface. The effect of the metals on the acceptor properties of the γ-Al_2O_3 is very strong. Thus, even assuming that the

¶T.V.Bychkova, E.V.Lunina, A.K.Selivanovskii, E.A.Nikel', T.Yu.Samgina, and B.V.Strakhov, Zhur.Fiz. Khim. (in press).

whole of the metal is in an atomic state and evenly distributed over the acceptor states (i.e. on the most favourable assumption) each metal atom has to block two acceptor centres at a metal concentration of 1×10^{13} atoms cm^{-2}. However, in real systems the deposited metals are known to be present as microcrystals. Therefore, the effectiveness of the suppression of surface acceptor centres by metal atoms is even greater than the above estimate. For example, in a sample containing 1.7 wt.% of platinum a single crystallite (average diameter 10 Å) can suppress the acceptor properties over an area 100 times greater than its own area, i.e. such a crystallite exhibits long-range effects. As has already been pointed out, the strength of the remaining acceptor centres also decreases very markedly.

Thus the application of the paramagnetic probe method in the study of bifunctional catalysts (Pt/Al_2O_3 and Pd/Al_2O_3) can yield technologically useful information on the interactions between the metal and the support.

On surfaces containing proton-donor centres as well as acceptor centres (for example, fluorinated Al_2O_3, alumina–silicas, decationated zeolites[11,19,38]) the radical (I) is unstable, and the concentration of acceptor centres is difficult to determine. The difficulty can be avoided by lowering the proton acidity (i.e. by exchanging the protons with alkali metal ions). This treatment stabilises the adsorbed radical (I) [19,33] without affecting the concentration of the acceptor centres, at least when the concentration of alkali metal ions is small[33].

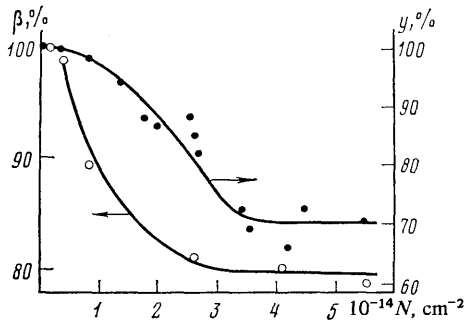


Figure 8. Dependence of the catalytic activity and of the acceptor capacity of γ-Al_2O_3 on the amount of cyclohexanol dehydrated on the catalyst surface at 150 °C: [34] y is the extent of conversion of the cyclohexanol, β is the acceptor capacity of the catalyst at the end of the experiment in arbitrary units (i.e. the contribution of the complex between radical (I) and the Al^{3+} ions to the overall ESR spectrum of the adsorbed radical (I).

VI. STUDY OF CATALYTIC PROCESSES

A very interesting possibility of the paramagnetic probe method is the study of the surface state of a catalyst during or immediately after the catalytic process. The radical (I) has been used[18,34] to indicate changes in the acceptor strength of a catalyst during the dehydration of an alcohol. Dehydration of isopropanol, n-butanol, and *t*-butanol was carried out in the adsorption layer of γ-Al_2O_3 at 100 °C.[18] The amount of alcohol adsorbed was sufficient to fill all the acceptor centres, with a slight excess. As a result of the dehydration reaction some of the acceptor centres were set free: the radicals (I) present on the surface were able to combine with these centres to form a complex. The freeing of the centres is due to the fact that the resulting alkenes are transferred to the gas phase, and water is less effective than alcohols in filling acceptor centres (see Table 3). All the acceptor centres are occupied when the amount of pre-adsorbed alcohol (and therefore the amount of water produced) is $(15 \pm 2) \times 10^{13}$ cm^{-2}. This value is almost the same as the concentration of water molecules needed to fill all the acceptor centres.

Thus, during the dehydration of alcohols the acceptor capacity of γ-Al_2O_3 is determined mainly by the concentration of water on the surface. This problem has been studied in detail[34], using as an example the dehydration of cyclohexanol on γ-Al_2O_3, and it was shown that a stationary catalytic activity and a stationary concentration of acceptor centres are set up during the catalytic experiment, depending only on temperature (Fig. 8). Evidently, the water produced by the dehydration reaction is partially desorbed from the surface, resulting in a steady state in which a definite concentration of catalytically active centres (Al^{3+} ions) remains invariant. As the temperature of the catalytic experiment decreases the desorption of water becomes more sluggish, lowering both the concentration of free acceptor centres and the catalytic activity of the sample.

The catalytic hydrogenation of di-*t*-butylnitroxyl on platinised silica gel and alumina surfaces has been studied[35] at −70 °C. The reaction product was the corresponding hydroxylamine:

$$(CH_3)_3C\diagdown\!\!\diagup N\!-\!\dot{O} + {}^1/_2 H_2 \rightarrow (CH_3)_3C\diagdown\!\!\diagup N\!-\!OH\ .$$

The progress of the reaction was monitored by ESR from the decrease in the concentration of radicals. Most of the results were obtained on SiO_2 (specific surface area $S = 340$ m^2 g^{-1}) containing 1.2% of Pt. The platinum was shown to be present as microcrystals containing an average of 5400 atoms. Therefore the average distance between Pt crystals on the surface was greater than 1000 Å. (Note that a distance of 100 Å is erroneously quoted in the original paper[35]). The coverage of the surface by the radical was fairly high ($\theta \cong 0.25$). Thus the distance between platinum crystals was almost two orders of magnitude greater than the distance between radicals. Therefore we could have expected the dehydration to be confined to those molecules in the immediate vicinity of Pt crystals, keeping the distance between the unreacted molecules constant. However, the ESR spectral changes during the hydrogenation (at −70 °C) indicate a uniform decrease in the concentration of the radical over the entire surface, i.e. an increase in the average distance between radicals. This observation implies a fairly high mobility of the particles in the adsorption layer, even at −70 °C. However, the mobile adsorbate (the radical, or an active form of hydrogen) has not yet been identified.

Nitroxyl radicals, though usually added to catalytic systems as probes or as reactants, can be generated on the surface by certain processes. The simplest is the oxidation of the corresponding hydroxylamine. It has been shown[35] that the hydroxylamine produced by reducing di-*t*-butylnitroxyl adsorbed on platinised silica gel or Al_2O_3 can be oxidised back to the initial radical by oxygen at 25 °C. Under these conditions the concentration of the resulting nitroxyl is not more than 27% of the concentration of the initial radical. Surprisingly, the nitroxyl prepared by oxidising a hydroxylamine on platinised Al_2O_3 is adsorbed on hydroxyl groups rather than on Al^{3+} ions. Apparently the Al^{3+} ions, having interacted with the initial radicals, are blocked by the water molecules produced by the oxidation.

Another, more interesting, and far more usual case is the formation of nitroxyl radicals from nitroso compounds and nitrones by free radical capture. In this way the short-lived radicals formed as intermediates by various reactions can be exploited. The method, which so far has been applied mainly in studies of homogeneous systems[36-38], has been called the spin trap method. In principle this method should give interesting information on reactions in heterogeneous systems.

The interation of *t*-nitrosobutane (TNB) with the activated surface of various oxides has been studied in our laboratory[39,40]. In these experiments the TNB was, simultaneously a reactant undergoing free-radical decomposition and a spin trap:

$$(CH_3)_3C{-}NO \xrightarrow{cat.} (CH_3)_3C^{\cdot} + NO$$
$$(CH_3)_3C^{\cdot} + (CH_3)_3C{-}NO \rightarrow (CH_3)_3C{-}\underset{\underset{O^{\cdot}}{|}}{N}{-}C(CH_3)_3 .$$

The experiments were carried out at room temperature in the dark in order to eliminate the side-reaction (decomposition of the TNB under the influence of light). The nitroxyl radicals produced by the above reaction can easily capture alkyl radicals with formation of diamagnetic adducts:

$$(CH_3)_3C^{\cdot} + (CH_3)_3C{-}\underset{\underset{O^{\cdot}}{|}}{N}{-}C(CH_3)_3 \rightarrow (CH_3)_3{-}\underset{\underset{C(CH_3)_3}{|}}{\overset{\overset{O}{|}}{N}}{-}C(CH_3)_3 ,$$

Therefore the activity of the catalysts towards the radical decomposition of TNB was estimated from the initial portion of the kinetic curve describing the formation of nitroxyl radicals, in which the latter reaction can be ignored.

Catalytic free-radical decomposition of TNB is observed on the surface of many oxides: MgO, ZnO, γ-Al_2O_3, Ga_2O_3, Y_2O_3, Sc_2O_3, La_2O_3, and SiO_2. It was shown[39,40] that the reaction occurs most readily on the surface of oxides having semiconductor properties, less readily on γ-Al_2O_3, and is almost undetectable on silica gel. These observations led to the hypothesis that the electron-donor centres on the surface are responsible for the radical decomposition process. The structure of the trapped butyl radical depends on the nature of the surface: on all the oxides except Al_2O_3 and Sc_2O_3 it is the normal *t*-butyl radical, formed by the decomposition of TNB. On γ-Al_2O_3 and Sc_2O_3 surfaces the *t*-butyl radical undergoes isomerisation to isobutyl, but the mechanism of this process has not yet been studied in detail.

The nitroxyl radicals formed by the radical decomposition of TNB also act as paramagnetic probes, and thus allow us to characterise the state of the surface. For example, the ESR spectra of these radicals formed on the surface of γ-Al_2O_3, Ga_2O_3, Sc_2O_3, and La_2O_3 include additional HFS from the nuclei ^{27}Al ($I_{Al} = 5/2$), $^{69,71}Ga$ ($I_{Ga} = 3/2$), ^{45}Sc, and ^{139}La ($I = 7/2$) respectively, i.e. the formation of donor–acceptor complexes is observed. Whereas on γ-Al_2O_3 and Ga_2O_3 these complexes can be produced by the adsorption of synthetic di-*t*-butylnitroxyl, this could not be done with Sc_2O_3 and La_2O_3. A probable explanation is that the Sc^{3+} and La^{3+} surface cations are available for the adsorption of nitroxyl radicals only during the catalytic decomposition of TNB.

These results highlight the importance of the spin trap method in studies of the mechanism of catalytic reactions and of the surface structure of working catalysts.

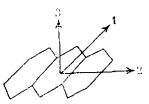
VII. STUDY OF THE DYNAMICS OF THE ADSORPTION LAYER

Information on the dynamics of the adsorption layer is highly relevant to an understanding of adsorption and catalytic processes. For example, if the surface mobility of the reactants is limited the effective rate constant of heterogeneous catalytic reactions is found[41] to be a function of the surface diffusion coefficient (i.e. of the velocity of translational motion). The velocity of rotation of the adsorbed molecules should also affect the rate of bimolecular catalytic reactions. For bimolecular reactions in rigid polymeric matrices this correlation between the rates of reaction and of molecular rotation has been established[42-44]. In the case of the bimolecular disproportionation of nitroxyl radicals adsorbed on alumina–silica the rate of the catalytic process was found to be determined by the mobility of the adsorbed molecules[19].

Studies of the mobility of adsorbed molecules are experimentally difficult, but significant advances have been made by the application of radio-frequency spectroscopy methods (and especially ESR).

The intensity of the rotational motion of the molecules is traditionally characterised by the correlation time $\tau_C = 1/\nu$, where ν is the rotation frequency[4]. By modelling the experimental spectra on a computer the correlation times describing the rotational mobility of the adsorbed molecules can be evaluated. This type of analysis of the ESR spectra of the cation radicals of polycyclic hydrocarbons adsorbed on alumina–silica[45] has shown that the rotation rates are quite high and the rotation is almost axially symmetrical (Table 4).

Table 4. Correlation times for the rotation of polycyclic hydrocarbon cation radicals adsorbed on alumina–silica[45].



Adsorbate	$10^{10}\tau_C$, s		
	τ_{C_1}	τ_{C_2}	τ_{C_3}
Perylene	27.5	3.9	2.75
Anthracene	21	2.1	2.1
Tetracene	42	3.5	2.8

Table 5. Correlation times τ_C for the rotation of radical (I) adsorbed from the vapour on SiO_2 at 20 °C.[23]

Adsorbent	S, $m^2 g^{-1}$	Pore radius, A	$10^9\tau_C$, s	
			$T_a = 170$° C	$T_a = 470$° C
Silica gel	660	15; 35	7.0	7.0
Silica gel	365	45	6.2	6.2
Silica gel	200	93	6.8	6.8
Aerosil	130	—	6.0	6.2

Advances in our understanding of the shape of the ESR spectra of nitroxyl radicals have led to the development of simple procedures for calculating the correlation times for rotation over the whole range of characteristic times accessible to the ESR method: $10^{-11} < \tau_C < 10^{-7}$ s.[3,4] The correlation time for rotation in non-viscous solutions is less than 10^{-11} s. Adsorption on SiO_2 surfaces strongly inhibits the rotation of nitroxyl radicals (as compared with a solution)[6,46]. The rotational mobility of the radical (I) is practically independent of both the structural characteristics of the SiO_2 surface and the vacuum activation temperature of the adsorbent in the range 150–800 °C [23] (see Table 5). Throughtout this review the anisotropy of the rotation of adsorbed nitroxyl radicals will be ignored.

The HFS components of the ESR spectra of radical (I) for samples activated at lower temperatures were found to be significantly broader than those of high-temperature samples[23]. Line broadening in low-temperature samples is probably due to the fact that the observed spectrum is a sum of spectra corresponding to different values of τ_C. This may be a consequence of the presence of different types of adsorption centre. The narrowing of the spectrum in SiO_2 samples activated at high temperatures suggests greater uniformity of the adsorption centres after high-temperature treatment.

The distribution of correlation times for the rotation of di-*t*-butylnitroxyl adsorbed on SiO_2 is clearly demonstrated in Ref.47. At low microwave powers (i.e. far from saturation) the contribution from slowly rotating molecules is predominant in the ESR spectra. At higher microwave power levels (under conditions of saturation) the major contribution comes from rapidly rotating molecules, whose rate of rotation is approximately 5 times greater. The presence of radicals differing in rate of rotation by more than 4 orders of magnitude on the SiO_2 surface (from $\tau_C > 10^{-5}$ to $\tau_C \cong 3 \times 10^{-9}$ s) has been demonstrated by the fast adiabatic pass method.

The activation energy for the rotation of the radical (I) on the surface of SiO_2 is ~2 kcal mole^{-1}.[46] A similar value (1.9 kcal mole^{-1}) is obtained for di-*t*-butylnitroxyl[6]. Allowing for the distribution of the correlation times of di-*t*-butylnitroxyl molecules Mailer and Hoffman[47] quote a value of 1.5 kcal mole^{-1} for the activation energy of rotation of the rapidly rotating molecules.

A non-polar solvent (toluene) increases the rotational mobility of the adsorbed radical (I), τ_C decreasing from 7.0×10^{-9} to 2.5×10^{-9} s.[46] This effect probably stems from a decrease in the non-specific interaction between the hydrophobic part of radical (I) and the surface.

a single value of τ_C is observed, also decreasing with increase of θ.

Sistovaris and coworkers[9] have studied the rotational mobility of different nitroxyl radicals adsorbed and "stitched" to the surface of SiO_2 samples which had been modified by "grafting" to the OH groups fragments such as $-(CH_2)_n-X$ (where X = H or NH_2, and $n = 2-8$). As the length of the hydrocarbon chain separating the paramagnetic $>\dot{N}-O$ fragment from the adsorption centre was increased the activation energy for rotation decreased from 8–10 to 2–5 kcal mole^{-1}. Non-polar solvents have almost no effect on the rate of rotation of the tracer (the paramagnetic fragment). Addition of a polar solvent increases the rotational mobility. The effect is most marked when the coverage of the surface by the polar solvent is a maximum.

Fox and coworkers[49] have used the paramagnetic probe method to study the adsorption of polymers from solution on SiO_2. From the ESR spectra of polymers labelled with nitroxyl radicals they were able to estimate the fractional number of segments actually adsorbed on the solid surface. Two values of the correlation time of the nitroxyl label are observed in the ESR spectra of these systems: a longer one, corresponding to slow rotation of the labels attached to segments of the polymer chain fixed to the surface, and a shorter one, corresponding to the faster motion of the chain fragments not bound to the surface.

When nitroxyl radicals are adsorbed on γ-Al_2O_3 or alumina–silica surfaces they form a complex with the Al^{3+} ions (as we have already pointed out) whose ESR spectrum is shown in Fig.2*a*. Lozos and Hoffman[6] estimate that the τ_C value for the rotation of di-*t*-butylnitroxyl in this case is close to the value for SiO_2 samples (6×10^{-9} s), with an activation energy for rotation of 1 kcal mole^{-1} (i.e. one-half the value for SiO_2).

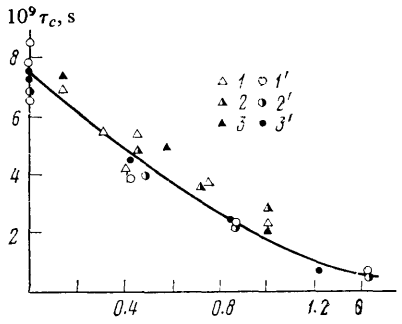


Figure 9. Mean correlation time (τ_C) for the rotation of radical (I) adsorbed on SiO_2 against coverage of the surface by adsorbed donor molecules (θ), from Ref.48: *1–3* adsorption of water, *1′–3′* adsorption of pyridine. Activation temperature of the SiO_2: 150 °C (*1* and *1′*), 300 °C (*2* and *2′*), 470 °C (*3* and *3′*).

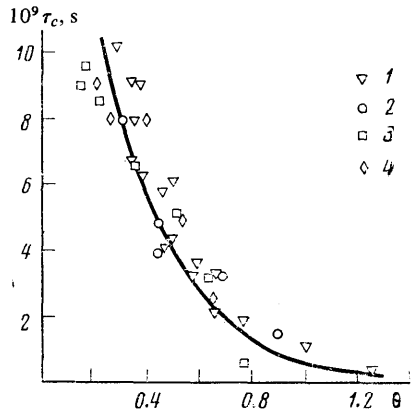


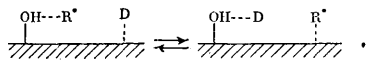
Figure 10. Mean correlation time (τ_C) for the rotation of radical (I) adsorbed on γ-Al_2O_3 ($T_a = 470$ °C) against coverage of the surface by adsorbed donor molecules (θ), from Ref.48. Adsorption: *1*) water, *2*) pyridine, *3*) n-butylamine, *4*) ammonia.

As we have already pointed out, donor adsorbates can displace the radical (I) from the surface OH groups. At surface coverages by donor molecules of $\theta \leq 0.7$ the rotational correlation times fall into two groups[48], corresponding to slow rotation of the specifically adsorbed radicals and fast rotation of the physisorbed radicals. As θ increases the proportion of physisorbed radicals increases, and the average value of τ_C correspondingly decreases (Fig.9). When $\theta > 0.7$

As in the case of the SiO_2 adsorbent, the rotational mobility of radical (I) adsorbed on activated γ-Al_2O_3 increases in the presence of a non-polar solvent (toluene)[14]. When donor molecules are adsorbed, radical (I) is displaced from the specific adsorption centres (first from the acceptor centres,

and then from the OH groups)[48]. At surface coverages of $0.3 \leq \theta \leq 1$ (as in the case of SiO_2) two forms of adsorption are observed: specific (on OH groups) and physical. Different values of τ_c apply to these forms. As θ increases the mean value of τ_c decreases because of the increased contribution from the rapidly rotating physisorbed molecules (Fig.10), and when $\theta > 1$ only one value of τ_c is observed.

These observations (the presence of one or two values of τ_c, or more probably of one or two groups of values of τ_c) can be explained by postulating an exchange between the adsorbate molecules:



In this scheme R· is a radical and D is a molecule of donor adsorbate. If this exchange is quite fast the system will have a single mean value of τ_c for rotation. The rate of exchange can be decreased by lowering the temperature of the sample. Under these conditions the ESR spectra yield two values of τ_c.[48] The situation is reversible: on raising the temperature the ESR spectrum can again be characterised by a single value of τ_c.

Thus, at the higher temperatures the life time of a molecule on an adsorption centre and the correlation time for rotation become comparable. Under these conditions it is meaningless to specify only rotational or only translational motion of the molecules, and it is more rational to consider a single rotational–translational motion. On the other hand if the molecule has a fairly long settled life time in its adsorption centre, and only seldom "jumps" from centre to centre, the two motions (rotational, and translational) can be considered separately.

ESR spectra are sensitive to the distance between the paramagnetic particles. From the dipole–dipole broadening of the spectra the average distance between nitroxyl radicals is found to be between 10 and 60 Å.[50] The time dependence of the average distance between adsorbed radicals has been used to characterise the translational mobility of the radicals.

An analysis[51] of the spectra of radical (I) adsorbed on SiO_2 has shown that the adsorption is initially very non-uniform, the distance between the nearest radicals being much smaller than the average distance. As a result of surface diffusion at room temperature these distances increase. The rate of surface diffusion is practically independent of the porosity and specific surface area of the silica gel sample. On raising the activation temperature of the sorbent the rate of increase diffusion decreases sharply. An estimate of the translational diffusion coefficients of radical (I) adsorbed on SiO_2 by the Einstein–Smoluchowsky equation gave value 12–15 orders of magnitude lower than in non-viscous liquids (10^{-20}–10^{-17} $cm^2\ s^{-1}$)[23].

In the presence of donor molecules (water, pyridine, alcohols, etc.) the translational mobility of radical (I) on a SiO_2 surface is sharply increased[48]. At a coverage by donor molecules of $\theta \cong 0.8$, and a mean distance between the radicals (I) of about 40 Å, the frequency of mutual collisions between the radicals becomes so high that exchange interaction becomes noticeable in the spectrum, as in the case of solutions in non-viscous solvents. Under these conditions the mobility of the molecules in the adsorption layer is comparable to the mobility of molecules in solution.

Because of the presence of acceptor centres the specific adsorption properties of γ-Al_2O_3 are much more marked than those of SiO_2. The radical (I) is adsorbed very non-uniformly on an activated γ-Al_2O_3 surface[52]. Localised concentrations of the radical (I) tend to disappear by surface diffusion, but whereas on SiO_2 this process is completed in a few hours at room temperature, on γ-Al_2O_3 it is still in progress after several days. The activation energy for surface diffusion is 29 ± 6 kcal $mole^{-1}$.[23] This value is close to the energy of the bond between the $\geq N-\dot{O}$ group and the acceptor centre, because this bond has to be broken when the radical (I) "jumps" from centre to centre.

The translational mobility of radical (I) adsorbed on γ-Al_2O_3 is increased (as in the case of the SiO_2 adsorbent) by the addition of donor molecules to the system[18,52]. The donor molecules displace the radical (I) from the acceptor centres, and a triplet component corresponding to radicals which are adsorbed but not complexed with Al^{3+} ions appears in the ESR spectrum as soon as a small addition of donor vapour is made to the system. Surface migration enables these radicals to form new complexes with the acceptor centres which are still free, and a spectrum similar to that shown in Fig.2*a* is gradually re-established. As a result the radical (I) becomes more evenly distributed over the surface. The relatively fast changes in the system come to an end when the radicals have become attached to the acceptor centres.

If the concentration of donor molecules is increased all the acceptor centres are occupied and some of the radicals (I) are unable to form complexes with the Al^{3+} ions: under these conditions a stable triplet appears in the ESR spectrum. The relative amounts of radical (I) which are (respectively) complexed or displaced from the acceptor centres are independent of the order in which the radical and the donor molecules were added to the system. They are determined only by the amount and the nature of the donor adsorbate, i.e. an equilibrium distribution of radical (I) and of the second donor adsorbate is gradually established over the adsorption centres of the γ-Al_2O_3.

The mobility of molecules of bases on the γ-Al_2O_3 surface can be studied by using NO as an indicator of free acceptor centres[29]. After the adsorption of 7×10^{13} cm^{-2} molecules of pyridine (i.e. almost double the amount needed to fill all the acceptor centres) a large number of free acceptor centres is observed during the first few hours in the ESR spectra of NO. Therefore the adsorption of pyridine is very non-uniform, with a large proportion of the adsorbate molecules on the outer surface of the adsorbent grains, leaving the internal surfaces free. Redistribution of the adsorbate over the surface takes place gradually, and after several days all the acceptor centres are occupied by pyridine molecules.

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Thus the paramagnetic probe method is likely to find increasing application in studies of adsorption and catalysis. It gives clear indications of the formation of an adsorption layer, and of its dynamics, and it can be used to characterise the interaction between adsorbed molecules and the active centres of the surface, i.e. to solve the fundamental problems in the physical chemistry of heterogeneous catalysis.

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Doubly Stabilised Chalcogenonium Ylides

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A systematic and general account is given of the methods of synthesis, structures, and reactivities of sulphur, selenium, and tellurium ylides containing two strongly electron-accepting substituents at the ylide carbon atom. The bibliography includes 166 references.

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I. INTRODUCTION

Recently there has been a considerable growth of interest in ylides—compounds in which the positive charge of the onium group is stabilised by a neighbouring carbanion. This class of compounds is of interest from both theoretical (characteristics of steric and electronic structures and reactivity) and practical points of view. The importance of the Wittig reaction[1] (interaction of phosphonium ylides with carbonyl compounds), whereby one can obtain olefins with a wide variety of structures, is generally known. Sulphonium ylides of different types, which have been examined in a monograph[2], are widely used together with the ylides of other elements for the synthesis of oxirans, cyclopropanes, and five- and six-membered heterocyclic compounds.

However, the sharp increase of the number of publications on sulphonium ylides together with the appearance of communications on the synthesis and properties of their analogues in terms of Mendeleev's Table—the selenonium and telluronium ylides—made necessary a systematic account and a more detailed examination of data obtained for individual classes of chalcogenonium ylides. In the first place, one must distinguish ylides stabilised by two electron-accepting groups capable of delocalising the negative charge of the carbanion; subsequently, such ylides will be called, for brevity, doubly stabilised (distabilised) ylides (DSY). Ylides of this type, which were believed previously to be chemically inert, subsequently began to attract the attention of chemists, because it was found that they react fairly readily with different electrophiles, enter into thermolytic and transylidation reactions, undergo various rearrangements, etc., and in terms of their reactivity they frequently differ significantly from other types of ylides. In many instances the mode of reaction of doubly stabilised chalcogenonium ylides is extremely unusual and is characteristic only of such ylides, which leads to new possibilities for syntheses based on them. The unusual nature of the methods of their synthesis and reactivity requires a separate consideration of ylides of this type.

This review does not deal with carbonyl ylides, i.e. oxygen ylides. This is because, in contrast to chalcogenonium ylides, the oxygen ylides are merely short-lived extremely reactive intermediates and because both these and other related ylides have been examined in a recent review[3].

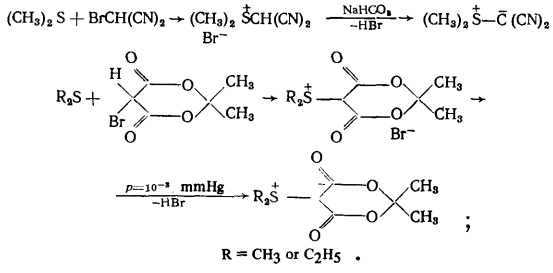
II. METHODS OF SYNTHESIS

The methods of synthesis of the DSY of Group VI elements known at present are in many respects analogous to the procedures found previously for the synthesis of the ylides of Group V elements. At the same time specific methods have been developed recently for the synthesis of DSY which can evidently find applications in the synthesis of selenonium and telluronium ylides. The fundamental problem in the formation of the DSY of Group VI elements is the synthesis of the chalcogenonium component; we therefore based our classification of the methods of synthesis of DSY on the nature of the chalcogenonium component.

1. Ylides from Diorganochalcogenides R^1R^2M (M = S, Se, or Te)

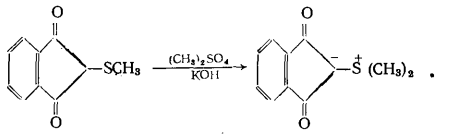
(a) The Salt Method

The salt method is one of the main procedures for the synthesis of non-stabilised and singly stabilised ylides of Group V [1] and VI [2] elements; it is based on the interaction with bases of onium salts containing at least one hydrogen atom at an α-carbon atom. This method has been little used for the synthesis of the DSY of Group VI elements because of the low yields of ylides (owing to the instability of the corresponding chalcogenonium salts) and also because of the frequently poor availability of the initial salt. However, dimethylsulphonium dicyanomethylide[4] and dialkylsulphonium 2,2-dimethyl-4,6-dioxo-1,3-dioxanilides[5,6] have been obtained with the aid of this method:

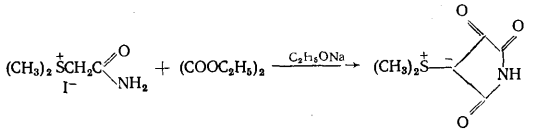


The instability of salts of the type $R_2S^+CHXYHal^-$ is probably associated with the highly electrophilic properties of the 'onium cations, which leads to their ready cleavage by the counterions (Hal^-). One should also note that, in the synthesis of such salts by the alkylation of sulphides by the halogeno-derivatives of active methylene compounds, the reaction apparently does not proceed unambiguously. At the

same time DSY have been synthesised successfully[7] by alkylating a sulphide containing two-electron-accepting groups with dimethyl sulphate in an alkaline medium:



DSY have been synthesised by introducing electron-accepting groups into a pre-existing sulphonium salt during the condensation of sulphonia-acetamides with oxalate esters in the presence of alkoxides[8]:



A specific version of the salt method has been used in the synthesis of sulphonium dinitromethylides[9]: it involves the interaction of dibromodinitromethane with a large excess of dimethyl sulphide or thiourea, which leads to the formation of relatively unstable crystalline compounds, which on treatment with water give rise to the ylides $(CH_3)_2\overset{+}{S}-\overline{C}(NO_2)_2$ and $(H_2N)_2C{=}\overset{+}{S}-\overline{C}(NO_2)_2$.

(b) The Formation of Ylides from Activated Oxirans

One of the most important methods of synthesis of dicyanomethylides involves the interaction of diorganosulphides[4,10–13] and diorganoselenides[14] with activated oxirans—tetracyanoethylene oxide[4,10,11,13] or 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene oxide[4,12] (Table 1):

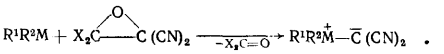
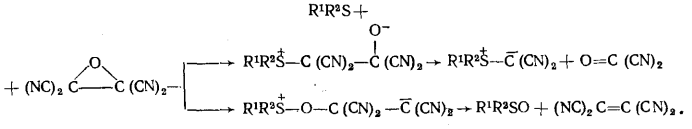


Table 1.

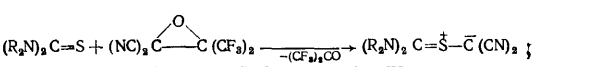
R^1	R^2	Refs.	R^1	R^2	Refs.
	$M = S,\ X = CN$			$(CH_2)_4$	[4]
CH_3	CH_3	[4, 10]		$(CH_2)_5$	[11]
C_2H_5	C_2H_5	[4]		$CH_2CH{=}CHCH_2$	[11]
C_3H_7	C_3H_7	[10]		$CH_2CH_2SCH_2CH_2$	[11]
C_4H_9	C_4H_9	[4]		$o\text{-}CH_2C_6H_4CH_2$	[11]
$C_6H_5CH_2$	$C_6H_5CH_2$	[11]		$o\text{-}CH_2CH_2C_6H_4$	[11]
C_6H_5	C_6H_5	[10]		$o\text{-}CH_2CH_2C_6H_4CH_2$	[11]
$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	[11]		$(H_2N)_2C{=}$	[13]
$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	[11]		$M = Se,\ X = CN$	
CH_3	C_2H_5	[11]	$C_6H_5CH_2$	$C_6H_5CH_2$	[14]
CH_3	C_3H_7	[11]	$4\text{-}CH_3C_6H_4CH_2$	$4\text{-}CH_3C_6H_4CH_2$	[14]
CH_3	$C_6H_5CH_2CH_2$	[11]		$M = S,\ X = CF_3$	
CH_3	$C_{12}H_{25}$	[4]	C_6H_5	C_6H_5	[4]
CH_3	C_6H_5	[4, 11]	CH_3	$C_{12}H_{25}$	[4]
CH_3	$1\text{-}C_{10}H_7$	[4]	CH_3	C_6H_5	[4]
CH_3	$4\text{-}CH_3OC_6H_4$	[4]	CH_3	$4\text{-}CH_3SC_6H_4$	[4]
CH_3	$4\text{-}BrC_6H_4$	[4]		$(CH_2)_4$	[4]
CH_3	$4\text{-}CH_3SC_6H_4$	[4]		$(H_2N)_2C{=}$	[12]
C_2H_5	C_6H_5	[4, 11]		$[(CH_3)_2N]_2C{=}$	[12]
C_4H_9	C_6H_5	[4]		$HNCH_2CH_2NHC{=}$	[12]
$C_6H_5CH_2$	C_6H_5	[11]			

The reaction can proceed via two different pathways and, depending on the nature of the groups at the sulphur atom, can lead to ylides or sulphoxides[11,13]:



The preferred pathway depends on steric factors—for bulky sulphides, the possibility of the reaction with carbon atoms shielded by the cyano-groups is hindered, so that the interaction involves the oxygen atom. The ease of formation of ylides diminishes in the sequence $Alk_2S > AlkSAr > Ar_2S$ and the yields of sulphoxides as a rule increase.

1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene oxide is a more convenient donor of the dicyanomethylene group than tetracyanoethylene oxide, since in its reactions hexafluoroacetone, which is less reactive than the dinitrile of mesoxalic acid, is split off. In the study of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene oxide, side reactions are therefore reduced to a minimum and the yield and purity of the resulting ylides (particularly those obtained from thiourea and its derivatives) are appreciably increased[12]:



(c) The Carbene Method

One of the comparatively new methods of synthesis of DSY is based on the reaction of highly electrophilic carbenes, obtained from the corresponding diazo-compounds by thermal or photochemical methods, with compounds of a bivalent chalcogen. The method, used mainly to synthesise sulphonium ylides, has been recently examined in a review[15] (Table 2):

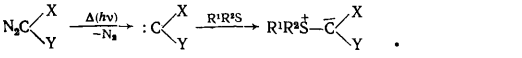


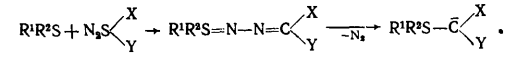
Table 2.

R^1	R^2	Refs.	R^1	R^2	Refs.
	$X = Y = SO_2C_6H_5$			$CBr{=}CHCH{=}CH$	[27]
CH_3	CH_3	[16]		$o\text{-}C_6H_4{-}CH_2CH_2$	[15, 21]
C_4H_9	C_4H_9	[16]		$X{=}Y{=}COOC_2H_5$	
CH_3	C_6H_5	[17]	CH_3	CH_3	[18, 20, 21]
	$X = Y = COOCH_3$		C_2H_5	C_2H_5	[22]
CH_3	CH_3	[18–25]	CH_3	C_4H_9	[21]
C_2H_5	C_2H_5	[18, 19, 21–23]	CH_3	$C_6H_5CH_2$	[21]
iso-C_3H_7	iso-C_3H_7	[18, 21]		$X = Y = COCH_3$	
C_6H_5	C_6H_5	[18, 21]	CH_3	CH_3	[18, 20, 21, 24, 29]
CH_3	C_6H_5	[18, 19, 21, 22, 24, 25]	CH_3	C_6H_5	[24]
CH_3	iso-C_3H_7	[24, 25]		$X{=}Y{=}COC_3H_7\text{-}iso$	
CH_3	n-H_9	[18, 19, 21, 24, 25]	CH_3	CH_3	[29]
CH_3	t-C_4H_9	[18, 19, 21]		$X{=}COCH_3$,	
CH_3	s-C_8H_{17}	[25]		$Y{=}COOCH_3$	
CH_3	$C_6H_5CH_2$	[18, 19, 21, 23–25]	CH_3	C_6H_5	[24]
CH_3	C_6H_5	[18, 19, 21, 24, 25]		$X{=}Y{=}CN$	
CH_3	$4\text{-}CH_3C_6H_4$	[17]	C_3H_7	C_3H_7	[11]
CH_3	CH_2COOCH_3	[21]	$C_6H_5CH_2$	$C_6H_5CH_2$	[11]
CH_3	CH_3SCH_2	[25]	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	[11]
CH_3	$CH_2COOC_2H_5$	[23]	$(CH_2)_5$		[11]
C_2H_5	CH_2COOCH_3	[23]	$CH_2CH_2SCH_2CH_2$		[11]
C_6H_5	n-C_4H_9	[21]	$o\text{-}CH_2C_6H_4CH_2$		[11]
$C_2H_5CH_2$	$4\text{-}CH_3C_6H_4$	[17]	$o\text{-}C_6H_4CH_2CH_2$		[11]
$(CH_2)_4$		[21]		$XY{=}$	
$(CH_2)_5$		[21]		$=COCH_2C(CH_3)_2CH_2CO$	
$(CH_2)_6$		[21]	CH_3	CH_3	[30]
$CH_2CH{=}CHCH_2$		[15]		$XY{=}C(O)OC(CH_3)_2OC(O)$	
$CH{=}CHCH{=}CH$		[15, 26–28]	CH_3	CH_3	[29]
$CCl{=}CHCH{=}CCl$		[27]			
$C(CH_2OH){=}CHCH{=}CH$		[27]			
$CBr{=}C(CH_3)CH{=}CH$		[27]			
$C(CH_3){=}CHCH{=}CH$		[27]			

The best yields of ylides are usually attained in the thermal generation of carbenes in the presence of anhydrous copper sulphate of copper powder, which reduce the decomposition temperatures of the diazo-compounds[18,21]. Thus, in

the photochemical decomposition of dimethyl diazomalonate in diphenyl sulphide, the corresponding diphenylsulphonium dimethoxycarbonylmethylide is obtained in 12% yield, while in the thermal decomposition the yield is 85%.[18,21] Furthermore, in the photochemical synthesis of the carbenes the yields of the ylides are greatly reduced when branched sulphides are used in the reaction[18,21]. It is also of interest that, according to the data of Nikolaev et al.[29], cyclic diazoketones completely fail to form sulphonium ylides in the course of their photolysis in alkyl sulphides—the resulting carbene merely undergoes the Wolff rearrangement. The reason for this is probably that the *trans*-disposition of the diazogroups and neighbouring substituents, which is fixed in the molecules of these diazoketones, ensures a higher (compared with acyclic diazoketones) capacity of the alkyl groups for migration (the Wolff rearrangement). In the photolysis of acyclic 2-diazo-1,3-diketones, the formation of the corresponding sulphur DSY is accompanied also by the formation of the products of the Wolff rearrangement, the product ratio depending on the bulk of the alkyl substituents in the ketone: an increase of the bulk of the substituents lowers the yield of the ylides[29].

The addition of a singlet carbene to the sulphur atom is postulated in the thermal and non-sensitised photochemical decomposition reactions of diazo-compounds[21]. At the same time, the ready formation of sulphonium ylides in the benzophenone-sensitised photolysis of dimethyl diazomalonate in alkyl sulphides is evidence, according to the authors[21], of the involvement of a triplet carbene in the reaction. The ylide can be formed either via the attack by the triplet carbene on the sulphur atom with subsequent inversion of spins or via a preliminary conversion of the triplet carbene into a singlet carbene in the presence of dialkyl sulphides with subsequent addition to the sulphur atom[21]. Nor can one rule out the possibility that the ylides are synthesised via the intermediate formation of sulphur azines[11], analogous to the formation of phosphine azines in the reaction of phosphines with diazo-compounds[31]:



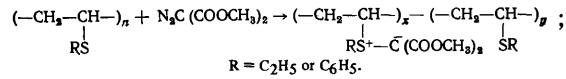
The use of dialkoxydisulphides[22] as catalysts makes it possible to obtain ylides from diazo-compounds at room temperature without irradiation. However, this method has no special advantages over the photochemical and even less so the thermal methods of generating ylides, because many ylides cannot be obtained by this method at all.

Unsaturated sulphides (allyl-, vinyl-, and ethynyl-substituted sulphides) are also capable of forming sulphonium ylides on reaction with carbenes[15,26,32]. However, the DSY derived from allyl sulphides readily undergo the allyl rearrangement[32–35] (see Section III), while in vinyl and ethynyl sulphides the sulphur is less reactive than in alkyl sulphides, owing to conjugation with the double or triple bond and it is therefore not always possible to obtain the sulphonium DSY.[26] Furthermore, the addition of carbenes to the double bond has been observed. Nevertheless, the carbene generated from dimethyl diazomalonate is "captured" by the weakly basic sulphur of thiophen (and its derivatives) or dibenzothiophen to give the corresponding S-ylides[15,21,26,27,28]. The sulphonium ylides formed from carbenes and four- or five-membered non-aromatic cyclic sulphides cannot be isolated, because they readily undergo the Stevens rearrangement with ring expansion; on the other hand, the ylides derived from six-membered sulphides are entirely stable[15,21,32].

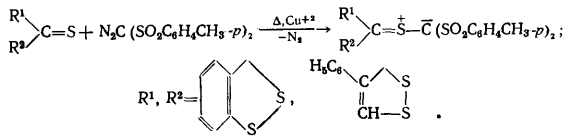
Table 3.

R¹	R²	Refs.
M=S		
X=Y=CONHCONHCO		
CH_3	CH_3	[6, 40–42]
C_2H_5	C_2H_5	[40]
$C_6H_5CH_2$	$C_6H_5CH_2$	[43]
CH_3	C_2H_5	[40]
$(CH_2)_4$		[40]
X=Y=CONHCON(CH₃)CO		
CH_3	CH_3	[40]
C_2H_5	C_2H_5	[40]
CH_3	C_2H_5	[40]
$(CH_2)_4$		[40]
X=Y=CON(CH₃)CON(CH₃)CO		
CH_3	CH_3	[40]
C_2H_5	C_2H_5	[40]
X=Y=*o*-COC_6H_4CO		
CH_3	CH_3	[6, 41, 43, 44]
C_2H_5	C_2H_5	[41]
C_6H_5	C_6H_5	[44]
CH_3	C_6H_5	[44]
CH_3	4-$CH_3OC_6H_4$	[44]
CH_3	4-BrC_6H_4	[44]
CH_3	4-ClC_6H_4	[44]
$(CH_2)_4$		[41]
X=Y=*o*-COC_6H_4COCO		
CH_3	CH_3	[40]
X=Y=1,8-$COC_{10}H_6CO$		
CH_3	CH_3	[6]
X=Y=$COOC(CH_3)_2OCO$		
CH_3	CH_3	[6]
C_2H_5	C_6H_5	[6]
$C_6H_5CH_2$	$C_6H_5CH_2$	[6]
C_6H_5	C_6H_5	[43]
CH_3	$C_6H_5CH_2$	[43]
X=Y=$COCH_2CH_2CH_2CO$		
CH_3	CH_3	[43]
CH_3	C_6H_5	[45, 46]
X=Y=$COOC(CH_3)_2CO$		
CH_3	CH_3	[43]
$C_6H_5CH_2$	$C_6H_5CH_2$	[43]
X=Y=$COCH_2C(CH_3)_2CH_2CO$		
CH_3	CH_3	[30, 41, 42, 45, 46]
$C_6H_5CH_2$	$C_6H_5CH_2$	[30]
CH_3	C_6H_5	[30, 45, 46]
$(CH_2)_4$		[41]
X=Y=COCONHCO		
CH_3	CH_3	[41]
X=Y=$SO_2C_6H_5$		
CH_3	CH_3	[40]
X=$COCH_3$, Y=$COOC_2H_5$		
CH_3	CH_3	[41, 45, 46]
CH_3	C_6H_5	[45, 46]
X=$COCH_3$, Y=$CONHC_6H_5$		
CH_3	CH_3	[41]
M=Se		
XY=$COCH_2C(CH_3)_2CH_2CO$		
CH_3	C_6H_5	[51]
CH_3	2-$CH_3OC_6H_4$	[51]
CH_3	1-$C_{10}H_7$	[51]
CH_3	2,4,6-$(CH_3)_3C_6H_2$	[51]
$C_6H_5CH_2$	C_6H_5	[51, 55]
X=Y=NO_2		
C_6H_5	C_6H_5	[52, 53]
X=Y=CN		
$C_6H_5CH_2$	$C_6H_5CH_2$	[54]
C_6H_5	C_6H_5	[54]
$(CH_2)_4$		[54]
$C_6H_5CH_2$	C_6H_5	[54]
X=Y=COC_6H_5		
C_6H_5	C_6H_5	[55]
X=NO_2, Y=$COOCH_3$		
C_6H_5	C_6H_5	[52, 53]
X=Y=$SO_2OC_6H_5$		
CH_3	CH_3	[47]
X=Y=NO_2		
CH_3	CH_3	[43, 48, 49]
C_2H_5	C_2H_5	[49]
$C_6H_5CH_2$	$C_6H_5CH_2$	[48]
C_6H_5	C_6H_5	[48]
X=Y=CN		
CH_3	CH_3	[6, 41, 42, 44–46]
C_2H_5	C_2H_5	[41]
CH_3	C_6H_5	[44–46]
CH_3	4-$CH_3OC_6H_4$	[44]
CH_3	4-ClC_6H_4	[44]
CH_3	4-BrC_6H_4	[44]
CH_3	4-$CH_3COC_6H_4$	[44]
X=Y=$COCH_3$		
CH_3	CH_3	[41, 45, 46]
C_3H_7	C_3H_7	[41]
CH_3	C_6H_5	[45, 46]
X=Y=$COOC_2H_5$		
CH_3	CH_3	[41]
X=$SO_2C_6H_5$, Y=COC_3H_5		
CH_3	CH_3	[30]
CH_3	C_6H_5	[30]
X=$SO_2CH=CH_2$, Y=$SO_2C_6H_5$		
CH_3	CH_3	[50]
X=NO_2, Y=CN		
CH_3	CH_3	[49]
X=NO_2, Y=$COCH_3$		
CH_3	CH_3	[49]
X=NO_2, Y=COC_6H_5		
CH_3	CH_3	[48]
X=NO_2, Y=$COOCH_3$		
CH_3	CH_3	[48, 49]
X=NO_2, Y=$CONH_2$		
CH_3	CH_3	[49]
X=CN, Y=$COCH_3$		
CH_3	CH_3	[41]
C_3H_7	C_3H_7	[41]
X=CN, Y=$COOC_2H_5$		
CH_3	CH_3	[45, 46]
CH_3	C_6H_5	[45, 46]
X=CN, Y=$PO(OC_2H_5)_2$		
CH_3	CH_3	[41]
X=$COCH_3$, Y=COC_6H_5		
CH_3	CH_3	[45, 46]
CH_3	C_6H_5	[45, 46]
X=NO_2, Y=COC_6H_5		
C_6H_5	C_6H_5	[52, 53]
X=CN, Y=$COOCH_3$		
$C_6H_5CH_2$	$C_6H_5CH_2$	[54]
$(CH_2)_4$		[54]
$C_6H_5CH_2$	C_6H_5	[54]
X=CF_3, Y=COC_6H_5		
C_6H_5	C_6H_5	[56]
$C_7H_5CH_2$	C_6H_5	[56]
X=SCH=CHCH=CCO, Y=$COCF_3$		
C_6H_5	C_6H_5	[56]
X=$COOCH_3$, Y=$COCOOCH_3$		
$C_6H_5CH_2$	$C_6H_5CH_2$	[14]
M=Te		
X=Y=$COCH_2C(CH_3)_2CH_2CO$		
4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	[57]
X=Y=*o*-COC_6H_4CO		
4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	[57]
X=Y=$COOC_2H_5$		
4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	[57]
X=NO_2, Y=$COOC_2H_5$		
4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	[57]

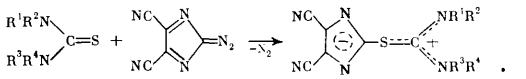
The synthesis of polyvinylsulphonium ylides should be mentioned[36]:



Thiocarbonyl compounds can also "capture" carbenes[37]:

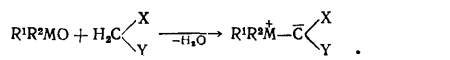


The high stability of thiocarbonyl ylides obtained from 4,5-dicyano-1,3-diazacyclopentadiene is also noteworthy[38,39]:



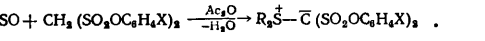
2. Synthesis from Diorganochalcogen Oxides R^1R^2MO (M = S, Se, or Te)

One of the most thoroughly developed methods for the synthesis of the DSY of Group VI elements involves the interaction of diorganochalcogen oxides with compounds containing active methylene groups (Table 3):

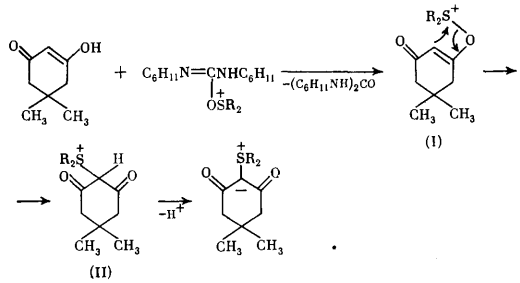


The course of the reaction and the yields of the ylides are influenced significantly by the basicity of the chalocogen oxides. Indeed, whereas in the case of sulphoxides dehydrating agents have to be used, frequently under relatively severe conditions [treatment with hot acetic anhydride[7], P_2O_5 in triethylamine[45,46], aryl cyanates[42], thionyl chloride[4], sulphur trioxide[49], and dicyclohexylcarbodi-imide (DCCD) in the presence of anhydrous phosphoric acid[41]], the more basic diaryl selenoxides[58] readily give rise to the corresponding ylides in the presence of acetic anhydride at room temperature[52,53], DCCD,[55,56] anhydrous sodium sulphate in chloroform[51,54], and (as in the case of diaryl telluroxides[57]) even in the absence of dehydrating agents[54]. The reactions of asymmetric selenoxides with dimedone in the presence of anhydrous sodium sulphate and 10-*d*-camphorsulphonic acid have been used to synthesis optically active selenonium ylides[51].

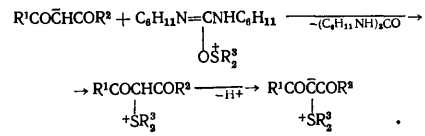
The C–H acidity of the active methylene compounds is also important. Thus, whereas fairly acidic compounds with active methylene groups form ylides, the less acidic compounds (phenylacetonitrile, fluorene, and tetraethyl methylenebisphosphonate) are inert under the usual reaction conditions[41]. However, in the synthesis of ylides from aryl esters of methionic acid, electron-donating substituents X in the aromatic ring, which lower acidity, promote the formation of ylides, while electron-accepting substituents hinder it (with X = *p*-NO_2, the reaction does not occur at all[47]):



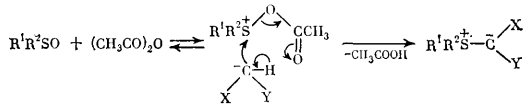
It has been suggested that, when DCCD is used, the reaction of sulphoxides with compounds containing active methylene groups proceeds via the intermediate formation of an adduct of the sulphoxide with DCCD; nucleophilic attack on the adduct by an enol gives rise to an enolsulphonium derivative (I). The latter rearranges to the diketosulphonium derivative (II) and, by losing a proton in a polar medium, is converted into the corresponding ylide[41]:



Another possible reaction mechanism involves the nucleophilic attack on the adduct by a carbanion with subsequent loss of a proton[41]:



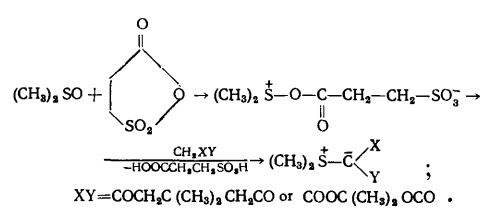
Ylides are formed via a similar mechanism from sulphoxides and active methylene compounds in acetic anhydride[6,46]:



It is of interest to note that, in contrast to diaryl sulphoxides, diaryl telluroxides react with acetic and other anhydrides to form the corresponding diacylates in quantitative yields[59,60].

The use of acetic anhydride as the dehydrating agent lowers the yields of sulphonium ylides somewhat as a consequence of a side reaction—the Pummerer reaction. The best results are therefore obtained, particularly in the case of dimethyl sulphoxide, when DCCD is used. In fact, whereas in the presence of acetic anhydride the malonic ester does not form an ylide with dimethyl sulphoxide and the cyanoacetic ester gives rise to an ylide in a yield of only 2%, in the presence of DCCD the yields of ylides greatly increase and amount to 40 and 62% respectively[41] (other examples have also been quoted[41]).

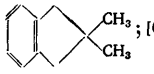
The inner anhydride of γ-sulphopropionic acid, which is apparently free from the disadvantages characteristic of acetic anhydride, has been recently proposed as the condensing agent for the synthesis of sulphonium ylides[61]. The betaine formed on interaction with the sulphoxide is made to react with active methylene compounds:



An unusual method of synthesis of the DSY of Group VI elements from diorganochalcogen oxides involves the interaction of the latter with dimethyl acetylenedicarboxylate[14,62,63] or tetracyanoethylene[14]:

$$R_2MO + CH_3OOCC \equiv CCOOCH_3 \rightarrow R_2\overset{+}{M}-\bar{C}\begin{matrix}COCOOCH_3\\COOCH_3\end{matrix}$$

M=S: R=CH_3 [62]; M=Se: R=$C_6H_5CH_2$ [14],



[63]

$$R_2SeO + (NC)_2C{=}C(CN)_2 \rightarrow R_2\overset{+}{Se}-\bar{C}(CN)_2\ ;$$

R=$C_6H_5CH_2$ [14] or p-$CH_3C_6H_4CH_2$,[14]

3. The Formation of Ylides from σ-Chalcogenuranes $R^1R^2MZ_2$ (Z = Hal)

The reaction of σ-selenuranes and σ-telluranes with active methylene compounds in the presence of bases has recently come to be used widely for the synthesis of selonium and telluronium ylides[55,64-69] (Table 4):

$$R^1R^2MZ_2 + CH_2\begin{matrix}X\\Y\end{matrix} \xrightarrow[-2HZ]{base} R^1R^2\overset{+}{M}-\bar{C}\begin{matrix}X\\Y\end{matrix}\ .$$

Table 4.

R^1	R^2	Refs.
M = Se, Z = Cl [55, 65—67], Br [64]		
X = Y = $COOC(CH_3)_2OCO$		
CH_3	CH_3	[64]
X = Y = $COCH_2C(CH_3)_2CH_2CO$		
C_6H_5	C_6H_5	[66]
$(CH_2)_4$		[66]
X = Y = $COCH_3$		
C_6H_5	C_6H_5	[66]
CH_3	C_6H_5	[66]
$(CH_2)_4$		[66]
X = Y = COC_6H_5		
CH_3	C_6H_5	[66]
$C_6H_5CH_2$	C_6H_5	[55]
$(CH_2)_4$		[66]
X = Y = CN		
CH_3	CH_3	[67]
C_6H_5	C_6H_5	[66]
CH_3	C_6H_5	[66]
$(CH_2)_4$		[66]
X = $COCH_3$, Y = COC_6H_5		
$C_6H_5CH_2$	C_6H_5	[55]
X = $COCH_3$, Y = $COOC_2H_5$		
$(CH_2)_4$		[66]
X = CN, Y = $COOCH_3$		
$(CH_2)_4$		[66]
X = CN, Y = $COOC_2H_5$		
$(CH_2)_4$		[66]
M = Te, Z = Cl, Br [68, 69]		
X = Y = $COCH_2C(CH_3)_2CH_2CO$		
CH_3	CH_3	[68, 69]
C_6H_5	C_6H_5	[68, 69]
4-$(CH_3)_2NC_6H_4$	4-$(CH_3)_2NC_6H_4$	[69]
4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	[68, 69]
4-$C_2H_5OC_6H_4$	4-$C_2H_5OC_6H_4$	[69]
4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	[68, 69]
4-FC_6H_4	4-FC_6H_4	[69]
4-BrC_6H_4	4-BrC_6H_4	[69]
CH_3	C_6H_5	[69]
CH_3	4-$CH_3OC_6H_4$	[69]
CH_3	4-$C_2H_5OC_6H_4$	[69]
CH_3	4-$CH_3C_6H_4$	[69]
4-$CH_3OC_6H_4$	4-$(CH_3)_2CHC_6H_4$	[69]
4-$CH_3OC_6H_4$	$C_6H_5CH_2$	[69]

Note. Here and in the other tables the numbers in square brackets denote references (Ed.of Translation).

This reaction is apparently inapplicable to the synthesis of sulphonium ylides—possibly because the corresponding σ-sulphuranes do not exist in the form of covalent structures with a bisphenoid bond configuration, like the selenium and tellurium compounds, but in the form of charge-transfer complexes[70,71]. In the synthesis of selenonium and telluronium ylides from σ-chalcogenuranes the bases employed were KOH in methanol[66], pyridine[66,67], triethylamine[64,68,69], and sodium ethoxide[55].

Another version of the use of σ-chalcogenuranes in the synthesis of DSY involves their interaction with two equivalents of the sodium salts of active methylene compounds[72]. This reaction, which so far has been investigated only in relation to a single example, can evidently involve the following mechanism:

$$(C_6H_5)_2SeCl_2 + NaCH(COCH_3)_2 \xrightarrow{-NaCl} (C_6H_5)_2\overset{+}{Se}CH(COCH_3)_2\ Cl^- \rightarrow$$
$$\xrightarrow[-NaCl,\,-CH_3(COCH_3)_2]{NaCH(COCH_3)_2} (C_6H_5)_2\overset{+}{Se}\bar{C}(COCH_3)_2\ .$$

4. Ylides Obtained from Alkoxy- and Aza-sulphonium Salts

A number of DSY of sulphur have been synthesised by the reaction of alkoxydiorganosulphonium fluoroborates[46] or perchlorates[73] with the sodium salts of active methylene compounds:

$$R^1R^2\overset{+}{S}-OC_2H_5Z^- + NaCH\begin{matrix}X\\Y\end{matrix} \xrightarrow[-C_2H_5OH]{-NaZ} R^1R^2\overset{+}{S}-\bar{C}\begin{matrix}X\\Y\end{matrix}\ ;$$

Z=BF_4^-, X=Y=$COCH_3$: R^1=R^2=CH_3 [46]; X=$COCH_3$, Y=COC_6H_5: R^1=CH_3, R^2=C_6H_5 [46];
X=$COCH_3$, Y=$COOC_2H_5$: R^1=CH_3, R^2=CH_3, R_2=CH_3 or C_6H_5 [46];
X=$COOC_2H_5$, Y=CN: R^1=CH_3 or C_6H_5 [46]
Z=ClO_4^-: X=Y=$COOCH_3$, R^1R^2=2.2′-$C_6H_4OC_6H_4$ [73]

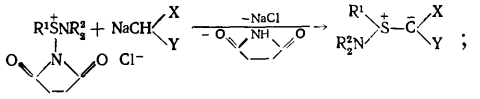
A more convenient modification of this method, not requiring the use of alkoxysulphonium salts prepared beforehand, involves the employment of t-butoxydiorganosulphonium chlorides obtained when sulphides are treated with t-butyl hypochlorite at low temperatures[74-77]:

$$R^1R^2S + t\text{-}BuOCl \rightarrow R^1R^2S\begin{matrix}Cl\\OBu\text{-}t\end{matrix} \xrightarrow[t\text{-}BuOH,\ -NaCl]{NaCHXY} R^1R^2\overset{+}{S}-\bar{C}\begin{matrix}X\\Y\end{matrix}\ ;$$

X=Y=$COOCH_3$: R^1=CH_3, R^2=2-$CH_3OC_6H_4$ [74], 2-$CH_3C_6H_4$ [74];
X=Y=CN: R^1=R^2=CH_3 [76] .

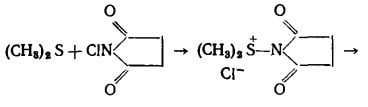
When the reaction is carried out in the presence of menthol, asymmetric induction takes place and optically active sulphonium ylides are obtained[74,75].

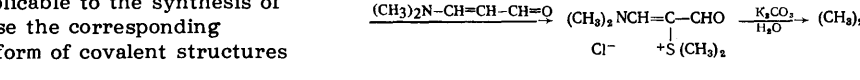
Azosulphonium salts behave similarly to alkoxysulphonium salts. Treatment of alkyl- or aryl-(dialkylamino)(succinimido)sulphonium chlorides[77,78] with sodio-derivatives of active methylene compounds leads to the corresponding ylides[77]:



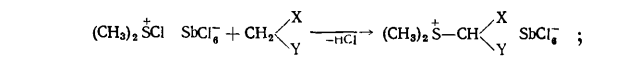
R^1=C_6H_5, R^2=CH_3 or R_2^2=$CH_2CH_2OCH_2CH_2$ or $(CH_2)_5$;
R^1=C_2H_5, R_2^2=$CH_2CH_2OCH_2CH_2$; X=$COOCH_3$, Y=$COOCH_3$, $COOC_2H_5$ [77]; X=Y=$C_6H_5SO_2$ or CH_3SO_2;
XY=$COCH_2C(CH_3)_2CH_2CO$ [77]

Another version of the method, with azasulphonium salts as intermediates in the synthesis of DSY, has been demonstrated[79]:





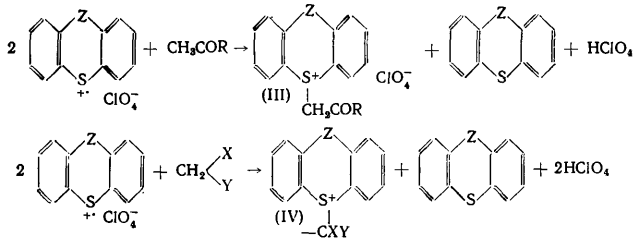
The conversion of diorganochlorosulphonium salts into compounds of the type $R_2\overset{+}{S}CHXYZ^-$, from which one can obtain, for example, sulphur-containing DSY, has been described[80]:



X=Y=CN; X, Y=CON(CH$_3$)CON(CH$_3$)CO .

5. Synthesis Via S-Radical-cations

A specific method of synthesising sulphur-containing DSY involves the interaction of the perchlorates of thianthrene and phenoxathi-in radical-cations with various keto-compounds, which lead either to β-ketosulphonium salts (III) or to sulphur-containing DSY (IV), depending on the nature of the keto-compounds:

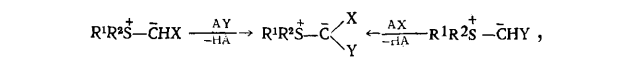


Z=O: X=Y=COCH$_3$ [82],
Z=S: X, Y=COCH$_2$C(CH$_3$)$_2$CH$_2$CO [81]; X=COC$_6$H$_5$, Y=COOC$_2$H$_5$ [81] .

It is noteworthy that in the case of dibenzoylmethane the product is the sulphonium salt (II) and not the ylide (IV), whose formation might have been expected by analogy with the reactions of acetylacetone and dimedone. It may be hoped that the reaction under consideration will be useful for the synthesis of chalcogenium ylides whose precursors are capable of forming radical-cations.

6. Preparation of Doubly Stabilised Ylides from Singly Stabilised Compounds

Doubly stabilised ylides of Group VI elements can be obtained by treating various singly stabilised ylides with electrophiles such as carboxylic acid anhydrides and chlorides, sulphonyl halides, isocyanates, and benzoyl isocyanates via the following mechanism:

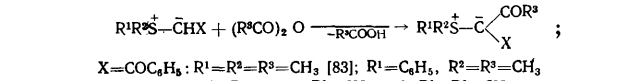


where X and Y are different electron-accepting groups.

The same DSY can be obtained in two ways via these reactions from different singly stabilised ylides and electrophiles. However, hitherto mainly sulphonium ylides have been obtained by this method.

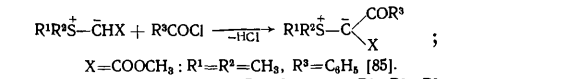
Acylation of Ylides

Singly stabilised sulphonium ylides containing the COOR, COR, and PO(OR)$_2$ substituents at the ylide carbon atom are smoothly acylated by carboxylic acid anhydrides with formation of sulphur DSY:



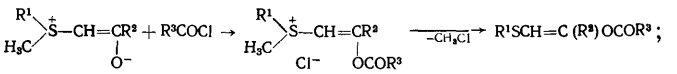
X=COC$_6$H$_5$: R^1=R^2=R^3=CH$_3$ [83]; R^1=C$_6$H$_5$, R^2=R^3=CH$_3$ [84]; R^1=R^3=C$_6$H$_5$, R^2=CH$_3$ [84]; R^1=R^2=CH$_3$, R^3=C$_6$H$_5$ [83, 85, 86]or iso-C$_4$H$_9$ [87]; R^1=R^2=C$_6$H$_5$, R^3=CH$_3$ [88]; R^1=R^3=CH$_3$, R^2=C$_2$H$_5$ [83]; R^1=CH$_3$, R^2=C$_2$H$_5$, R^3=C$_6$H$_5$ [83]; X=COOCH$_3$: R^1=R^2=CH$_3$, R^3=C$_6$H$_5$ [85], X=COOC$_2$H$_5$: R^1=R^2=R^3=C$_6$H$_5$ [89]; CH$_3$ [90], R^1=R^2=C$_6$H$_5$, R^3=CH$_3$ [89]; R^1=R^3=C$_6$H$_5$, R^2=CH$_3$ [89]; R^1=C$_6$H$_5$, R^2=R^3=CH$_3$ [89]; R^1=R^3=CH$_3$, R^2=C$_6$H$_5$ [90] X=PO(OC$_2$H$_5$)$_2$: R^1=R^2=CH$_3$, R^3=CH$_3$ or C$_6$H$_5$ [91] .

Carboxylic acid chlorides[85,90-92] and esters[92] react similarly to singly stabilised ylides containing the alkoxy carbonyl[85,89,90], diethoxyphosphoryl[91], and cyano-groups[92]:



X=COOCH$_3$: R^1=R^2=CH$_3$, R^3=C$_6$H$_5$ [85].
X=COOC$_2$H$_5$: R^1=R^2=CH$_3$, R^3=C$_6$H$_5$ [90]; R^1=R^2=R^3=C$_6$H$_5$ [89]; R^1=R^3=C$_6$H$_5$, R^2=CH$_3$ [89]; R^1=R^3=CH$_3$, R^2=C$_6$H$_5$ [89]; R^1=R^3=CH$_3$, R^3=C$_2$H$_5$ [90] or CHCl$_3$ [90].
X=PO(OC$_2$H$_5$)$_2$: R^1=R^2=CH$_3$, R^3=CH$_3$ or C$_6$H$_5$ [91];
X=CN: R^1=CH$_3$, R^2=C$_2$H$_5$, R^3=CH$_3$ or C$_6$H$_5$ [92] .

The behaviour of sulphonium ketoylides in interactions with acyl chlorides is unusual. As a consequence of the considerable contribution of resonance structures of the type $R_2S^+CH{=}C(R)O^-$, they usually yield *O*-acylation and not *C*-acylation products on treatment with acyl chlorides. In the presence of at least one methyl group at the onium sulphur atom, methyl chloride is in most cases eliminated from the resulting sulphonium salt and the products are enol acylates of the corresponding α-mercaptoketones[84-86]:

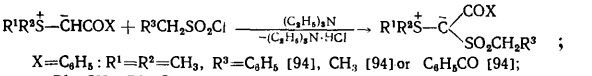


R^1=R^2=R^3=C$_6$H$_5$ [84]; R^1=R^2=C$_6$H$_5$, R^3=CH$_3$ [84];
R^1=CH$_3$, R^2=R^3=C$_6$H$_5$ [85, 86] .

On the other hand, the reaction involving diphenylsulphonium phenacylide stops at the stage involving the formation of the sulphonium salt[88].

The Sulphonation and Cyanation of Singly Stabilised Ylides

On treatment of alkoxycarbonyl- or keto-sulphonium ylides with alkanesulphonyl chlorides in the presence of triethylamine, the initial ylides are *C*-sulphonated with formation of sulphur DSY:[88,93,94]

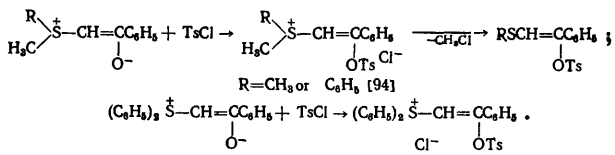


X=C$_6$H$_5$: R^1=R^2=CH$_3$, R^3=C$_6$H$_5$ [94], CH$_3$ [94]or C$_6$H$_5$CO [94];
R^1=CH$_3$, R^2=C$_6$H$_5$, R^3=H [94], CH$_3$ [94], C$_6$H$_5$ [94]or C$_6$H$_5$CO [94]; R^1=R^2=C$_6$H$_5$, R^3=H [88].
X=CH$_3$: R^1=R^3=CH$_3$, R^2=C$_6$H$_5$ [94]; R^1=R^3=C$_6$H$_5$, R^2=CH$_3$ [94].
X=OC$_2$H$_5$: R^1=R^3=CH$_3$, R^2=C$_6$H$_5$ [94]; R^1=R^3=C$_6$H$_5$, R^2=CH$_3$ [94]; R^1=R^2=C$_6$H$_5$, R^3=CH$_3$ [94] or C$_6$H$_5$ [94].

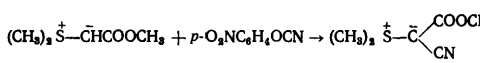
The yields of the doubly stabilised ylides are sometimes extremely low owing to the occurrence of many side reactions[94].

In contrast to aliphatic sulphonyl chlorides, aromatic sulphonyl chlorides (particularly the tosyl chloride) give rise to *O*- and not *C*-derivatives on reaction with sulphonium phenacylides. Dialkyl(arylalkyl) sulphonium ylides give rise to the enol sulphonates derived from α-mercaptoketones as a result of the elimination of methyl chloride from the

intermediate sulphonium salt[94], while diphenylsulphonium phenacylide yields the corresponding sulphonium salts[88]:



Cyanomethylides can be synthesised by the direct introduction of the cyano-group into singly stabilised ylides[95]:



Reactions of Singly Stabilised Ylides with Isocyanates

The interaction of singly stabilised ylides with isocyanates is widely used for the synthesis of DSY, since singly stabilised ylides containing different electron-accepting substituents at the carbanionic carbon atom readily undergo this reaction (Table 5):

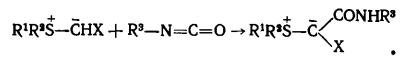
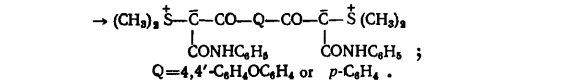


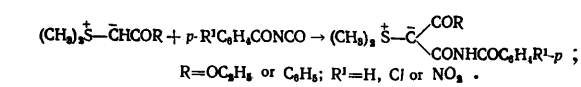
Table 5.

X	R^2	R^1	R^3	Refs.
COC_6H_5	C_6H_5	CH_3	CH_3	[83]
COC_6H_5	C_6H_5	CH_3	C_6H_5	[83]
COC_6H_5	C_6H_5	C_6H_5	$C_6H_5CH_2$	[46]
COC_6H_5	C_6H_5	C_6H_5	C_6H_5	[46]
COC_6H_5	C_6H_5	C_6H_5	CH_3	[84]
COC_6H_5	C_6H_5	$CH_3CH_2SCH_2CH_2$		[96]
COC_6H_5	C_6H_5	$CH_3SCH_2CH_2CH_2$		[96]
4-BrC_6H_4CO	C_6H_5	$CH_3CH_2SCH_2CH_2$		[96]
4-BrC_6H_4CO	C_6H_5	$CH_3SCH_2CH_2CH_2$		[96]
4-$O_2NC_6H_4CO$	C_6H_5	$CH_2CH_2SCH_2CH_2$		[96]
4-$O_2NC_6H_4CO$	C_6H_5	$CH_2SCH_2CH_2CH_2$		[96]
$COCH_3$	C_6H_5	C_6H_5	CH_3	[94]
$COCH_2C_6H_5$	C_6H_5	C_6H_5	CH_3	[94]
$COOC_2H_5$	C_6H_5	CH_3	CH_3	[90]
$COOC_2H_5$	C_6H_5	C_6H_5	C_6H_5	[89]
$PO(OC_2H_5)_2$	C_6H_5	CH_3	CH_3	[91]
$PO(OC_2H_5)_2$	C_6H_5	CH_3	C_6H_5	[91, 97]
$COOC_2H_5$	C_3H_7	CH_3	CH_3	[90]
$COOC_2H_5$	4-$CH_3C_6H_4SO_2$	CH_3	CH_3	[90]
4-$O_2NC_6H_4$	3,4-$Cl_2C_6H_3$	CH_3	CH_3	[98]
4-$O_2NC_6H_4$	C_2H_5OCO	CH_3	CH_3	[98]

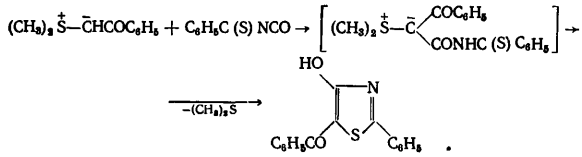
The reaction is sometimes used for the identification of comparatively unstable or difficult to purify ylides[94]. Chiral sulphonium DSY have been synthesised by this method from chiral singly stabilised ylides[83]. The reaction with isocyanates is suitable for the preparation of stable bis-DSY:[99]



Singly stabilised ylides also readily react with benzoyl isocyanates, giving rise to stable benzoylcarbamoylsulphonium ylides[100], whose pyrolysis in decalin leads to substituted oxazoles[100]:

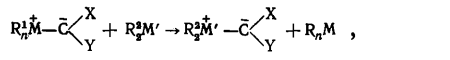


On the other hand, the interaction of dimethylsulphonium phenacylide with thiobenzoyl isocyanate even at room temperature immediately yields a substituted thiazole—via the decomposition of the intermediate ylide[100]:



7. Transylidation

The transylidation reaction involves the exchange of heteroatomic groups between the DSY of any elements and organochalcogenides:

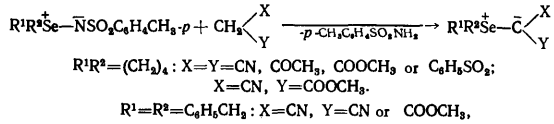


where M is the heteroatom and M′ the chalcogen (S, Se, or Te).

These reactions have found fairly limited applications in the synthesis of the DSY of Group VI elements and it is therefore more useful to consider them in the discussion of the chemical properties of the DSY.

8. Synthesis from Imides

A new method of synthesis of DSY by the reaction of active methylene compounds with comparatively readily available selenium imides has been proposed recently[54]:



The authors[54] note the absence of a linear correlation between the pK_a of the active methylene compounds and the rates of their reaction with selenium imides. Evidently, the stability of the resulting selenonium ylides plays a significant role here.

III. STRUCTURE AND PHYSICOCHEMICAL PROPERTIES

1. Molecular and Crystal Structure

The structures of six doubly stabilised chalcogenonium sulphur[27,41,101,102], selenium[72,103,104], and tellurium[105] ylides have now been investigated by X-ray diffraction, the results being presented in Figs. 1–6. They permit a number of conclusions.

A. As was to be expected, the DSY of Group VI elements have the structure of a trigonal pyramid containing the chalcogen atom at the vertex. On passing from sulphur to tellurium ylides, the distance from the central atom to the plane passing through three neighbouring atoms increases,

its values being as follows: 0.73 Å for (V), 0.74 Å for (VI), 0.78 Å for (VIII), 0.91 Å for (IX), and 0.98 Å for (X).

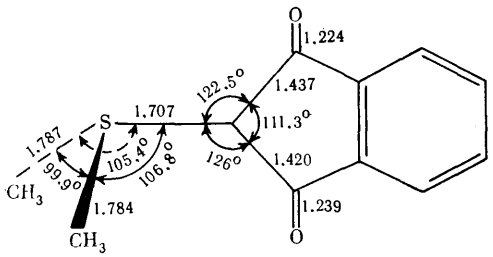


Figure 1. 2-Dimethylsulphuranylideneindan-1,3-dione (V).[102]

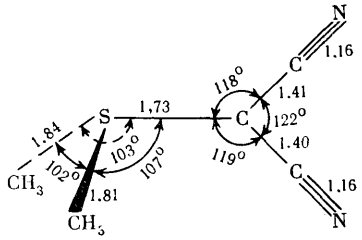


Figure 2. Dimethylsulphonium dicyanomethylide (VI).[41,101]

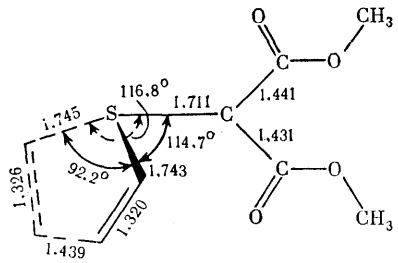


Figure 3. Thiophenium dimethoxycarbonylylide (VII).[27].

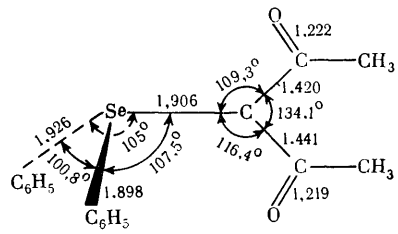
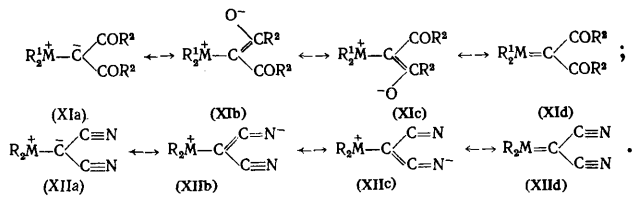


Figure 4. Diphenylselenonium diacetylmethylide (VIII).[72]

B. Analysis of the bond lengths between the chalcogen and the ylide carbon atom and of the bond lengths in the electronegative substituents C=O and C≡N (Figs. 1–6) shows that the electronegative groups play an important role in the delocalisation of the negative charge of the carbanion. In other words, the contribution of the resonance structures (XI, b and c) and (XII, b and c) to the ground state of the ylide molecules is important for diketo- and dicyano-methylides:



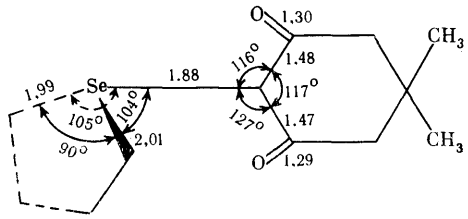


Figure 5. Tetramethyleneselenonium-4,4-dimethyl-2,6-dioxocyclohexanilide (IX).[103,104]

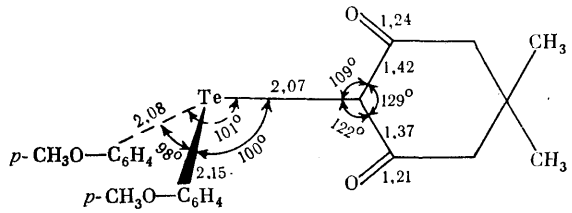


Figure 6. Di(*p*-anisyl)telluronium 4,4-dimethyl-2,6-dioxocyclohexanilide (X).[105]

A number of workers believe that the ylide linkage has a definite double bond character as a consequence of the employment of vacant *d* [101,102,104] or π* orbitals of sulphur and selenium[106].

C. In the case of selenium[104] and tellurium[105] dimedone ylides the oxygen atoms of the dimedone fragment are displaced from the plane of the ring in one direction or another by 0.15 and 0.24 Å (selenium) or 0.11 and 0.16 Å (tellurium) as a result of steric hindrance. Some non-equivalence of the arene rings in the ylide (X) is striking. This is manifested by the fact that one of the methoxy-oxygen atoms is displaced from the plane of the benzene ring by 0.16 Å, while the other lies in the plane of the corresponding ring. This is evidently a consequence of the bending of the dimedone ring, noted also for the corresponding selenonium ylide, and the characteristics of the crystal packing (particularly since in solution both benzene rings and methoxy-groups are completely equivalent judging from the ^{1}H NMR spectra[69]).

2. Ultraviolet Spectra

The ultraviolet spectra of doubly stabilised chalcogenonium ylides have been studied in a number of investigations[6,9,11,12,30,41,46,48,50,52,55,64,66,69,73,79,84,89,94], but these data have usually not been interpreted and the ultraviolet spectra of sulphonium ylides derived from dimedone and benzenesulphonylacetophenones have been examined in greater detail in only one study[30]. The authors[30] believe that the significant displacement of the maximum in the spectra of ylides relative to the spectra of the sodium salts of the initial carbonyl compounds is due to the shift of electron density in the carbanionic part of the ylide under the influence of the sulphuranylidene substituent. An analogous shift has been observed in the ultraviolet spectra of dinitromethylides[48].

Some data on the ultraviolet spectra of doubly stabilised chalcogenonium ylides are presented in Table 6. The replacement of the phenyl group by the methyl group leads to a bathochromic shift of the absorption band of the carbanionic fragment for all the chalcogenonium ylides—evidently as a consequence of the greater compensation of the positive charge on the chalcogen atom by alkyl substituents compared with the phenyl substituent. One should also note that, on passing from sulphur ylides to the selenium and tellurium ylides with similar structures, the long-wavelength absorption band of the ylides undergoes a bathochromic shift, probably as a consequence of the weakening of the electron-accepting properties of the groups R_2M^+ in the sequence $R_2S^+ > R_2Se^+ > R_2Te^+$.

Table 6. The ultraviolet spectra of the ylides $R^1R^2M^+C^-(X)Y$.

R^1	R^2	M	X	Y	λ_{max}, nm (solvent)
CH_3	CH_3	S	$-COCH_2C(CH_3)_2CH_2CO-$		261 [30, 41] (CH_3OH), 258 [46] (C_2H_5OH)
CH_3	CH_3	Te	$-COCH_2C(CH_3)_2CH_2CO-$		270 [69] (CH_3OH)
CH_3	CH_3	S	$-COOC(CH_3)_2OCO-$		247 [6, 64] (CH_3OH)
CH_3	CH_3	Se	$-COOC(CH_3)_2OCO-$		241 [64] (CH_3OH)
C_6H_5	CH_3	S	$-COCH_2C(CH_3)_2CH_2CO-$		230, 259 [30] (CH_3OH); 230, 257 [46] (C_2H_5OH)
C_6H_5	CH_3	Se	$-COCH_2C(CH_3)_2CH_2CO-$		261 [66]
C_6H_5	CH_3	Te	$-COCH_2C(CH_3)_2CH_2CO-$		268 [69] (CH_3OH)
C_6H_5	C_6H_5	S	$-COCH_2C(CH_3)_2CH_2CO-$		225, 250 [30] (CH_3OH)
C_6H_5	C_6H_5	Se	$-COCH_2C(CH_3)_2CH_2CO-$		257 [68]
C_6H_5	C_6H_5	Te	$-COCH_2C(CH_3)_2CH_2CO-$		262 [69] (CH_3OH)
CH_3	CH_3	S	$COCH_3$	$COCH_3$	233, 270 [46] (CH_3OH); 228, 271 [41] (H_2O)
C_6H_5	CH_3	S	$COCH_3$	$COCH_3$	226, 265 [46] (C_2H_5OH)
C_6H_5	CH_3	Se	$COCH_3$	$COCH_3$	268 [66]
C_6H_5	C_6H_5	Se	$COCH_3$	$COCH_3$	265 [66]
C_6H_5	CH_3	S	COC_6H_5	COC_6H_5	288, 317 [84] (C_2H_5OH)
C_6H_5	CH_3	Se	COC_6H_5	COC_6H_5	287, 317 [66]
CH_3	CH_3	S	COC_6H_5	$SO_2C_6H_5$	218, 266 [30] (CH_3OH); 218, 258 [94] (C_2H_5OH)
C_6H_5	CH_3	S	COC_6H_5	$SO_2C_6H_5$	218, 263 [30] (CH_3OH); 254 [94] (C_2H_5OH)
CH_3	CH_3	S	$COCH_3$	$COOC_2H_5$	227, 258 [46] (CH_3OH); 225, 247 [41] (C_2H_5OH)
C_6H_5	CH_3	S	$COCH_3$	$COOC_2H_5$	223, 247 [46] (C_2H_5OH)
CH_3	CH_3	S	$COOC_2H_5$	$COOC_2H_5$	233 [41] (C_2H_5OH)
CH_3	CH_3	S	$COOC_2H_5$	CN	223 [41] (CH_3OH)
C_6H_5	CH_3	Se	CN	CN	277 [66]
C_6H_5	C_6H_5	Se	CN	CN	257, 287 [66]
CH_3	CH_3	S	NO_2	NO_2	329 [9, 48] (CH_3CN)
C_6H_5	C_6H_5	Se	NO_2	NO_2	340 [53] (CH_3CN)

3. Infrared Spectra

The infrared spectra of doubly stabilised chalcogenonium ylides provide one of the most convincing pieces of evidence for the considerable involvement of electronegative substituents in the delocalisation of the negative charge on the ylide carbon atom[4,6,12,21,24,25,27,30,41,43,46,48,49,53,56,65,66,69,72,73,77,79,84,89,91,94].

The absorption frequencies of the electronegative substituents at the carbanionic carbon atom of ylides (COR, COOR, CN, NO_2, or SO_2R) are appreciably lower than in the spectra of the corresponding methylene compounds. If the ylide molecule contains two different electron-accepting substituents, the vibrations of the two groups can be usually readily distingiushed under these conditions. Certain vibrational frequencies of electronegative substituents in ylides are presented in Table 7.

Table 7. The vibrational frequencies of the substituents X and Y in the ylides $R^1R^2M^+-\bar{C}(X)Y$.

R^1	R^2	M	X	Y	ν(X, Y), cm^{-1}
CH_3	CH_3	S	$-COCH_2C(CH_3)_2CH_2CO-$		1560, 1602 [41], 1539 [46]
CH_3	CH_3	Te	$-COCH_2C(CH_3)_2CH_2CO-$		1535, 1590 [69]
C_6H_5	CH_3	S	$-COCH_2C(CH_3)_2CH_2CO-$		1570, 1610 [30]; 1572 [46]
C_6H_5	C_6H_5	S	$-COCH_2C(CH_3)_2CH_2CO-$		1567, 1582 [30]
C_6H_5	C_6H_5	Te	$-COCH_2C(CH_3)_2CH_2CO-$		1520, 1530, 1570 [69]
C_6H_5	$N(CH_3)_2$	S	$-COCH_2C(CH_3)_2CH_2CO-$		1580 [77]
C_6H_5	CH_3	Se	$-COCH_2C(CH_3)_2CH_2CO-$		1557, 1612 [66]
C_6H_5	C_6H_5	Se	$-COCH_2C(CH_3)_2CH_2CO-$		1563 [65, 66]
CH_3	CH_3	S	$COCH_3$	$COCH_3$	1560, 1605 [41]; 1570 [46]
C_6H_5	CH_3	S	$COCH_3$	$COCH_3$	1582 [46]
C_6H_5	$N(CH_3)_2$	S	$COCH_3$	$COCH_3$	1650 [77]
C_6H_5	CH_3	Se	$COCH_3$	$COCH_3$	1585, 1610 [66]
C_6H_5	C_6H_5	Se	$COCH_3$	$COCH_3$	1520 [72]; 1577, 1592, 1617 [66]
CH_3	CH_3	S	$COCH_3$	$COOC_2H_5$	1550, 1685 [41]; 1548, 1667 [46]
C_6H_5	CH_3	S	$COCH_3$	$COOC_2H_5$	1595, 1665 [46]
C_6H_5	C_6H_5	S	$COCH_3$	$COOC_2H_5$	1578, 1580 [89]
CH_3	CH_3	S	$COOC_2H_5$	$COOC_2H_5$	1635, 1670 [41]
CH_3	CH_3	S	$COOCH_3$	CN	1660, 2175 [41]
C_6H_5	CH_3	S	$COOC_2H_5$	CN	1660, 2180 [46]
CH_3	CH_3	S	CN	CN	2155, 2190 [41]
C_6H_5	CH_3	Se	CN	CN	2140, 2175 [66]
C_6H_5	C_6H_5	Se	CN	CN	2157, 2190 [66]
CH_3	CH_3	S	COC_6H_5	COC_6H_5	1545, 1577 [30]
C_6H_5	CH_3	S	COC_6H_5	$SO_2C_6H_5$	1560, 1583 [30]
C_6H_5	$N(CH_3)_2$	S	$SO_2C_6H_5$	$SO_2C_6H_5$	1133, 1300 [77]
C_6H_5	$N(CH_3)_2$	S	SO_2CH_3	SO_2CH_3	1116, 1283 [77]
CH_3	CH_3	S	NO_2	NO_2	1260, 1590 [43]; 1052, 1255, 1273, 1502 [48]
C_6H_5	C_6H_5	S	NO_2	NO_2	1062, 1280, 1505 [48]
C_6H_5	C_6H_5	Se	NO_2	NO_2	1270, 1490 [53]

It is noteworthy that the absorption frequencies of the same compounds quoted by different workers are frequently very different. This has been explained[108] by the existence of ketoylides in several stable conformations, which is strongly reflected in the infrared spectra (disappearance of individual absorption bands of CO or the appearance of new bands when the solvent or the state of aggregation of the given substance are altered).

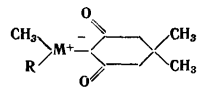
4. ^1H NMR and ^{13}C Spectra

The ^1H [6,30,41,43,46,54–56,69,94] and ^{13}C [24,29,48,111] NMR spectra of doubly stabilised chalcogenonium ylides make it possible to determine the characteristics of their steric and electronic structures. In particular the ^1H and ^{13}C NMR spectra of a number of ylides containing the benzyl, ethyl, and isopropyl groups at the chalcogen atom represent the AB spectrum of the methylene or methyl protons, while the methyl groups of the isopropyl substituent are manifested in the ^{13}C NMR spectrum of isopropylmethylsulphonium methoxycarbonylmethylide as doublets as a consequence of the trigonal-pyramidal structure of the ylide molecule. The magnetic non-equivalence of chemically identical methylene protons and methyl groups of the isopropyl substituent is due to the influence of the solvent[41,69,94]. Indeed, p-anisylbenzyltelluronium 4,4-dimethyl-2,6-dioxocyclohexylide in

methylene chloride gives rise to a signal of the methylene group of the benzyl substituent in the form of a narrow singlet, while in nitrobenzene solution the expected AB spectrum is obtained[69]. The difference between the chemical shifts of the magnetically non-equivalent protons usually diminishes with increase of the number of bonds between the chalcogen atom and the protons active in NMR.[41,69,94,109]

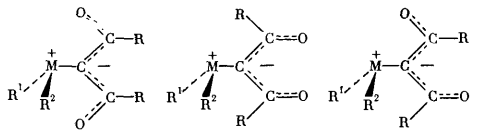
It is of interest to follow the variation of the chemical shifts of the signals due to the methyl groups in dimethyl- and phenylmethyl-chalcogenonium ylides, which have structures of the same type. The available data concerning this problem refer solely to dimedone ylides and are compiled in Table 8. The data presented in Table 8 show that, on passing from sulphur to tellurium, the deshielding effect of the groups RM^+-C^- diminishes, which can be evidently attributed to the weakening of the electron-accepting properties of the groups quoted above on moving from above downwards within the limits of a single Group in Mendeleev's Table.

Table 8. The chemical shifts of the protons of the methyl group in the ^1H NMR spectra of the ylides



R	M	δ_{CH_3}, p.p.m.
C_6H_5	S	3.34 [30]
C_6H_5	Se	3.10 [66]
C_6H_5	Te	2.65 [69]

The question of the conformations of acyclic diketoylides, which can exist in solution as one conformer or a mixture of three possible conformers (XIII, a–c) formed on rotation about the C^-–C bonds, has been raised in a number of studies:



(XIIIa) (XIIIb) (XIIIc)

On the basis of data for the temperature variation of the ^1H NMR spectrum of dimethylsulphonium diacetylmethylide (a singlet due to the acetyl methyls at room temperature and a doublet with an integral intensity ratio of 1 : 1 at −60 °C), the *cis,cis*-conformation (XIIIa) was attributed to this ylide in solution[46]. Despite the repulsion of the two methyl groups, the stabilisation of this conformer is caused, according to the authors, by the strong Coulombic interaction of the unlike charges on the oxygen and sulphur atoms. When one of the acetyl methyl groups is replaced by the bulky mesityl residue, the corresponding ylide exists in solution as a mixture of two conformers—*cis,cis* (XIIIa) and *cis,trans* (XIIIc) in proportions of 1 : 1 at temperatures between −50° and +50 °C.

The broadening of the signals of the acetyl methyl groups in the ^1H NMR spectrum of dimethylsulphonium diacetylmethylide at −25 °C made it possible to estimate the energy barrier to rotation about the S^+-C^- bond as 50 kJ mol^{-1}.[72] In the diphenylselenonium analogue of this ylide, the broadening of the signal due to the methyl groups was not observed even at −60 °C, which shows that the height of the barrier to rotation about the Se^+-C^- bond is less than 41.9 kJ mol^{-1}.[72] The above data (showing that the barrier to rotation in selenonium ylides is lower than in the sulphonium ylides) are consistent with the results of quantum-chemical calculations on different π-chalcogenuranes (oxides, imides, and ylides) and with the fact that in the sulphur–selenium–tellurium series the barriers to rotation about the M^+-C^- or M^+-N^- bonds are lowered, while the barriers to the inversion of the pyramid at the onium atom increase[110].

Table 9. The ^{13}C NMR spectra of the ylides $R^1R^2M^+-C^-(X)Y$.

R^1	R^2	M	X	Y	δ, p.p.m. (w.r.t. TMS) δ_{C^-}	$\delta_{C=O}$	$\delta_{CH_3-M^+}$	Refs.
CH_3	CH_3	S	COC_6H_5	COC_6H_5	88.2[a]	190.9	26.9	[24]
CH_3	CH_3	S	$COCH_3$	$COCH_3$	87.6[a]	190.3	26.7	[24]
CH_3	CH_3	S	$COCH_3$	$COOCH_3$	73.5[a]	166.4; 191.8	26.6	[24]
CH_3	CH_3	S	$COCH_3$	$COOCH_3$	73.4[b]	166.0; 189.9	26.0	[24]
CH_3	CH_3	S	$COOCH_3$	$COOCH_3$	58.6[a]	166.6	27.6	[24]
CH_3	CH_3	S	$COOCH_3$	$COOCH_3$	58.6[b]	165.6	27.1	[24]
CH_3	C_2H_5	S	$COCH_3$	$COOCH_3$	55.7[a]	—	27.7	[24]
CH_3	C_4H_9	S	$COOCH_3$	$COOCH_3$	56.2[a]	167.1	25.9	[24]
CH_3	$(CH_3)_2CH$	S	$COOCH_3$	$COOCH_3$	53.5[a]	167.2	24.4	[24]
CH_3	$C_6H_5CH_2$	S	$COOCH_3$	$COOCH_3$	57.4[a]	167.4	27.7	[24]
CH_3	C_6H_5	S	$COOCH_3$	$COOCH_3$	59.1[a]	167.1	27.1	[24]
$4\text{-}(CH_3)_2NC_6H_4$	$4\text{-}(CH_3)_2NC_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		51.3[c]	190.9	—	[111]
$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		51.4[c]	191.3	—	[111]
$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		52.7[d]	191.8	—	[111]
$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		51.3[c]	190.8	—	[111]
C_6H_5	C_6H_5	Te	$-COCH_2C(CH_3)_2CH_2CO-$		51.2[c]	190.7	—	[111]
$4\text{-}BrC_6H_4$	$4\text{-}BrC_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		51.3[c]	191.2	—	[111]
CH_3	$4\text{-}CH_3C_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		51.3[c]	191.6	3.0	[111]
CH_3	C_6H_5	Te	$-COCH_2C(CH_3)_2CH_2CO-$		51.2[c]	191.4	2.0	[111]
CH_3	CH_3	Te	$-COCH_2C(CH_3)_2CH_2CO-$		52.6[c]	192.3	1.2	[111]
CH_3	CH_3	S	$-COCH_2(CH_3)_2CH_2CO-$		86.1[a]	191.9	25.5	[29]
CH_3	CH_3	Se	NO_2	NO_2	124,7[b]	—	26.8	[48]

*Solvents: [a] $CDCl_3$; [b] DMSO-d_6; [c] $CHCl_3$; [d] acetone.

The ^{13}C NMR spectra of doubly stabilised chalcogenonium ylides have been very little investigated[24,29,48,111]. Certain data on these spectra are presented in Table 9, from which follow certain results of interest for the chemistry of ylides.

A. The signal of the ylide carbon atom in dialkoxycarbonylmethylides shifts upfield relative to diketoylides, which indicates a greater contribution of the betaine structures to the ground state of diketoylides compared with dialkoxycarbonylmethylides.

B. Whereas the chemical shift of the ylide carbon atom in sulphonium ylides is independent of the nature of the solvent, in telluronium ylides it varies by approximately 1.5 p.p.m. on passing from chloroform to acetone. This may be an indication of the greater basicity of the telluronium ylides compared with sulphonium ylides.

C. In chalcogenonium ylides containing isotypical electronegative substituents at the ylide carbon atom the chemical shift of the latter is displaced upfield on passing from sulphur to tellurium.

D. The chemical shift of the carbon atom of the methyl group in methylphenyltelluronium ylides (1–3 p.p.m.), which can be accounted for by the influence of the heavy atom, and the pronounced paramagnetic shift of the signal of the ylide carbon atom in *S*-dinitromethylide, located in the region of the signal of the carbon of the dinitrocarbon, are striking[48].

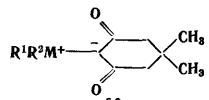
5. The Basicity of Ylides

In contrast to the singly stabilised sulphur ylides[112–114], no systematic studies have been made on the basicity of the series of doubly stabilised sulphonium and selenonium ylides. There exist only scattered data on the pK_a of sulphonium[7,55,115–119] and selenonium[48,120] ylides. It has been shown on the basis of spectroscopic data that sulphonium dimethoxycarbonylmethylides are protonated at the carbon atom[115], while the sulphonium dimedone ylides are protonated at the oxygen atom[118]; sulphonium diphenylacylmethylides[116] and acetylethoxycarbonylmethylides[117] are protonated at both oxygen and carbon atoms. Selenonium diketoylides are protonated at the oxygen atom[120], while sulphonium and selenonium dinitromethylides are protonated at the carbon atom[48].

The basicities of a systematic series of diorganotelluronium ylides have been determined[69] (Table 10) and the correlation between the basicity constants of diaryltelluronium ylides and the polar influence of the substituents has been investigated using different types of σ constants. The data in Table 10 show that the telluronium dimedone ylides are relatively strong bases, whose strength is comparable to that of aromatic amines. Indeed the pK_a for diphenyltelluronium dimedone ylide (10.59) is virtually equal to the pK_a of aniline determined under identical conditions[122]. It is of interest to compare the basicities of the DSY of Group VI elements differing only by the onium atom. Table 10 shows that the basicity of the ylides increases in the sequence S < Se < Te, i.e. with decrease of the electronegativity of the onium atom and with increase of its size. These data are consistent with the determinations of the basicities of the ylides of Group V elements having structures of the same type (the arsenic ylides are more basic than the phosphorus ylides[113]).

The best correlation in the case of symmetrical diaryltelluronium dimedone ylides is obtained using σ^0 constants[69] (the constants of substituents free from polar conjugation), although usually in the interaction of substituents with an electron-deficient centre the best correlation is observed when the electrophilic constants of the substituents are employed[123]. This permits the conclusion that the *p*-substituents in the arene rings interact with the onium tellurium atom mainly via an inductive mechanism[69]. It is noteworthy that many workers arrived at an analogous conclusion on the basis of the pK_a for singly stabilised sulphonium ylides. The data of Goetz et al.[44], who concluded that there is an appreciable mesomeric interaction between the benzene rings and the onium tellurium atom on the basis of a comparison of calculated and measured dipole moments of a series of sulphonium dicyano- and indandione ylides, therefore appear doubtful.

Table 10. The pK_a of the ylides



in acetonitrile at 25 °C.[69]

R^1	R^2	M	pK_a^T
4-$(CH_3)_2NC_6H_4$	4-$(CH_3)_2NC_6H_4$	Te	11.48[a]
4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	Te	10.74
4-$C_2H_5OC_6H_4$	4-$C_2H_5CO_6H_4$	Te	10.86
4-$CH_3C_6H_4$	4-$CH_3C_6H_6$	Te	10.69
C_6H_5	C_6H_5	Te	10.59
C_6H_5	C_6H_5	Se	9.59
4-FC_6H_4	4-FC_6H_4	Te	10.22
4-BrC_6H_4	4-BrC_6H_4	Te	10.07
4-$(CH_3)_2CHC_6H_4$	4-$CH_3OC_6H_4$	Te	10.69
C_6H_5	CH_3	Te	11.22
4-$CH_3OC_6H_4$	CH_3	Te	11.40
4-$C_2H_5OC_6H_4$	CH_3	Te	11.25
CH_3	CH_3	Te	12.07
CH_3	CH_3	S	9.67

[a] the second $pK_a^T = 6.61$.

6. Dipole Moments

Comparatively few studies have been made on the dipole moments of the doubly stabilised chalcogenonium ylides[4,44,69,120]. The available literature data on the dipole moments of the DSY of Group VI elements are presented in Table 11. The relatively low dipole moments of diketochalcogenonium ylides[69,120], in the range 2–5 D, are striking. The authors[69] explained this by the fact that the M^+-C^- and C=O bond moments in ylides of this type are pointing in different directions and to a large extent cancel out. Indeed, sulphonium dicyanomethylides, in which the moments of the S^+-C^- and C≡N polar bonds are pointing in the same direction and hence undergo vector addition, have higher dipole moments (7–8 D).[4,44] Quantum chemical calculations on certain dimethylsulphonium and dimethyl selenonium ylides[111] confirmed these hypotheses.

On the basis of the experimental dipole moments of ylides, the ylide bond moments have been calculated in a number of studies[44,120]. However, very drastic assumptions were then made, which greatly diminishes the reliability of the results, In fact, the ylide bond moments were obtained by subtracting from the experimental dipole moment of the ylide $R^1R^2M^+-C^-(X)Y$ the sum of the moments of the corresponding diorganochalcogenide R^1R^2M and the precursor of the carbanionic fragment of the ylide $H_2C(X)Y$, ignoring thereby the significant changes in the M–C and C–X and C–Y bond moments on passing from isolated molecules to ylides where considerable charges appear on the chalcogen and carbon atoms.

7. Mass Spectra

In contrast to the mass spectra of the doubly stabilised sulphonium ylides, those of diketoselenonium[124] and telluronium dimedone ylides[111] have been investigated in fair detail. Without going into the details of the mode of fragmentation of these ylides, which are in many respects similar in all cases, we may note the following features of the mass-spectrometric behaviour of the selenonium and telluronium ylides.

Table 11. The dipole moments of the ylides $R^1R^2M^+-C^-(X)Y$.

R^1	R^2	M	X	Y	μ, D	Refs.
4-$(CH_3)_2NC_6H_4$	4-$(CH_3)_2NC_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		5.49	[69]
4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		4.16	[69]
4-$C_2H_5OC_6H_4$	4-$C_2H_5OC_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		4.26	[69]
4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		3.58	[69]
C_6H_5	C_6H_5	Te	$-COCH_2C(CH_3)_2CH_2CO-$		3.16	[69]
4-BrC_6H_4	4-BrC_6H_4	Te	$-COCH_2C(CH_3)_2CH_2CO-$		1.74	[69]
4-FC_6H_4	4-FC_6H_4	Te	$-COCH_2C(CH_3)_2CH_2CO-$		2.06	[69]
CH_3	C_6H_5	Te	$-COCH_2C(CH_3)_2CH_2CO-$		2.90	[69]
CH_3	4-$CH_3OC_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		3.28	[69]
CH_3	4-$C_2H_5OC_6H_4$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		3.42	[69]
CH_3	CH_3	Te	$-COCH_2C(CH_3)_2CH_2CO-$		3.18	[69]
4-$CH_3OC_6H_4$	4-$(CH_3)_2CHC_6H_5$	Te	$-COCH_2C(CH_3)_2CH_2CO-$		4.05	[69]
CH_3	CH_3	S	CN	CN	7.40	[44]
C_4H_9	C_4H_9	S	CN	CN	7.7	[4]
C_6H_5	C_6H_5	S	CN	CN	7.6	[4]
CH_3	1-$C_{10}H_7$	S	CN	CN	8.1	[4]
CH_3	C_6H_5	S	CN	CN	8.24	[44]
CH_3	4-$CH_3OC_6H_4$	S	CN	CN	8.38	[44]
CH_3	4-ClC_6H_4	S	CN	CN	7.38	[44]
CH_3	4-BrC_6H_6	S	CN	CN	7.30	[44]
CH_3	4-$CH_3COC_6H_4$	S	CN	CN	6.94	[44]
CH_3	CH_3	S	o-COC_6H_4CO-		3.96	[44]
C_6H_5	C_6H_5	S	o-COC_6H_4CO-		4.09	[44]
CH_3	C_6H_5	S	o-COC_6H_4CO-		4.32	[44]
CH_3	4-$CH_3OC_6H_4$	S	o-COC_6H_4CO-		4.79	[44]
CH_3	4-ClC_6H_4	S	o-COC_6H_4CO-		4.18	[44]
CH_3	4-BrC_6H_4	S	o-COC_6H_4CO-		3.45	[44]
CH_3	C_6H_5	Se	COC_6H_5	COC_6H_5	3.38	[120]
	$-(CH_2)_4$	Se	COC_6H_5	COC_6H_5	3.27	[120]

A. The stability of the molecular ions of the ylides depends on the structure of the carbanionic fragment. Among the diketoylides (diacetyl and dibenzoylmethylides, dimedone ylides), the dimedone derivatives are the most resistant to electron impact[124].

B. The intensity of the molecular ion peaks in the total ionic current of the molecules depends in many respects on the nature of the chalcogen atom. Whereas the intensity of the molecular ionic peak is 0.1% in the case of diphenyl- and methylphenyl-telluronium dimedone ylides, the intensities of their selenonium analogues are 25.9 and 14.8% respectively.

C. The mass spectra of the selenonium ylides are characterised by the presence of rearranged ions, formed via the migration of the group linked to the selenium atom to the oxygen atom of the carbanionic fragment. Ions of this type are hardly observed in the mass spectra of tellurium-containing dimedone ylides[69,111]. This difference in the behaviour of selenonium and telluronium ylides is comparable to their behaviour in thermolysis (see below).

IV. CHEMICAL PROPERTIES

The reactivities of the doubly stabilised ylides of Group VI elements differ appreciably from those of the singly stabilised ylides. The significant diminution of the nucleophilic properties of the DSY compared with the singly stabilised ylides results in the failure of the DSY of Group VI elements to enter into reactions characteristic of singly stabilised ylides such as those with aldehydes, ketones, nitrosobenzene, etc.[1,2] On the other hand, they undergo a whole series of other reactions characterising the unusual features of ylides of this class.

Certain DSY, for example diorganosulphonium dicyanomethylides[4], diorganosulphonium dinitromethylides[48], organodialkylaminosulphonium ylides[77], and diorganotelluronium dimedone ylides[69], are highly stable compounds resistant to the action of alcohols[4], water[4,69,77], and aqueous solutions of alkalis[69]. On the other hand, certain other DSY readily react with these nucleophiles[17,53]:

$$C_6H_5(CH_3)\overset{+}{S}-\bar{C}(SO_2C_6H_5)_2 \xrightarrow[CH_3OH]{KOH} C_6H_5SCH(SO_2C_6H_5)_2 + CH_3OCH_3\ ;$$

$$n\text{-}CH_3C_6H_4(R)\overset{+}{S}-\bar{C}(COOCH_3)_2 \xrightarrow[CH_3OH]{KOH} n\text{-}CH_3C_6H_4SCH_2COOH + ROCH_3\ ;$$

R=CH_3 or $C_6H_5CH_2$ [17];

$$(C_6H_5)_2\overset{+}{S}e-\bar{C}(NO_2)X \xrightarrow{H_2O} (C_6H_5)_2SeO + XCH_2NO_2\ ;$$

X=NO_2, $COOCH_3$ or COC_6H_5 [53].

Reactions with fairly strong electrophiles and with compounds containing multiple bonds, thermolysis, rearrangements (the Stevens, Pummerer, and allyl rearrangements), transylidation, and certain other reactions are the most characteristic of the doubly stabilised chalcogenonium ylides.

1. Reactions With Electrophiles

(a) Interaction With Acids

Weak inorganic acids in most cases do not have an effect on the DSY, whereas strong inorganic acids readily react with them, the nature of the interaction depending both on the nature of the substituents at the ylide carbon atom and on the reaction conditions. Thus, whereas sulphonium dicyanomethylides[4] are cleaved by sulphuric acid in the cold into sulphides and unidentified products, the treatment of the same ylides in benzene with gaseous HX (X = Cl or Br) results in the formation of salts having the composition $R_2S^+-\bar{C}(CH)_2 \cdot 2HCl$.[119]

Sulphonium[48,125,126], and selenonium[53] dinitromethylides are protonated by strong acids containing weakly nucleophilic anions, giving rise to the corresponding salts:

$$R_2\overset{+}{M}-\bar{C}(NO_2)_2 + HX \rightarrow R_2\overset{+}{M}-CH(NO_2)_2\ X^-\ ;$$

M=S or Se; $X^-=SO_3F^-$, BF_4^- or HSO_4^-.

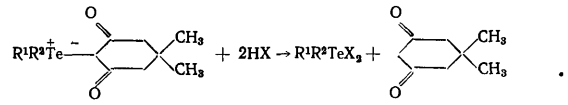
However, when sulphonium and selenonium dinitromethylides are treated with acids having highly nucleophilic anions, the M^+-C^- bond is ruptured. The intermediate onium salt is then capable of being cleaved both by the counterion (pathway *a*) and by yet another electrophile molecule (pathway *b*):[63,107,125,126]

$$R_2\overset{+}{M}-\bar{C}(NO_2)_2 \overset{HX}{\rightarrow} R_2\overset{+}{M}-CH(NO_2)_2\ X^- \begin{cases} \xrightarrow{a} R_2M + XCH(NO_2)_2 \\ \xrightarrow[HX]{b} R_2MX_2 + CH_2(NO_2)_2 \end{cases};$$

M=S or Se; X=Cl or Br.

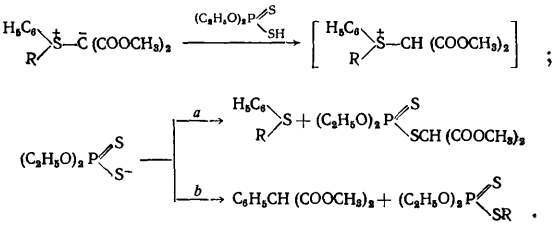
In the case of sulphonium dinitromethylides the reaction proceeds almost wholly via pathway *a*, while in the case of the selenonium compounds both pathways are followed to an approximately equal extent. The enhancement of the nucleophilic properties of the counterion (on passing from HCl to HBr) tends to increase the yield of the nucleophilic cleavage products (pathway *a*). On the other hand, tellurium-containing dimedone ylides always give rise to the corresponding σ-telluranes and dimedone on treatment with HX (X = F, Cl,

Br, or I) regardless of the nature of the substituents at the tellurium atom[127]:



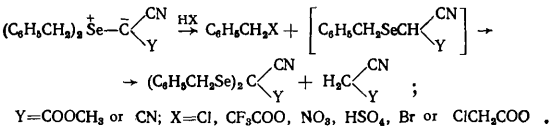
The ability to be cleaved via pathway *b* has hitherto been observed only for DSY. The ease of this process increases in the sequence S < Se < Te, which is probably associated with the greater stability of the tetracoordinate derivatives of tellurium and selenium compared with the analogous sulphur compounds[70,71].

When sulphonium dimethoxycarbonylmethylides are treated with HBr [25] or diethyl hydrogen phosphorodithioate[128], the reaction proceeds with the dissociation of either the S^+-C^- or $R-S^+$ bond depending on the nature of the substituent R at the onium sulphur:



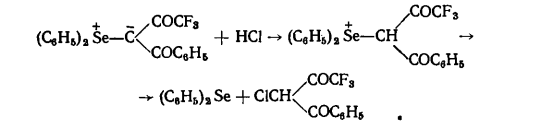
When R = C_6H_5, pathway *a* is followed exclusively, in the presence of R = $C_6H_5CH_2$ pathway *b* is followed exclusively, while in the presence of R = CH_3 both pathways are used to an equal extent.

Dibenzylselenonium dicyanomethylides are cleaved by various acids only at the $C_6H_5CH_2-Se^+$ bond[129]:

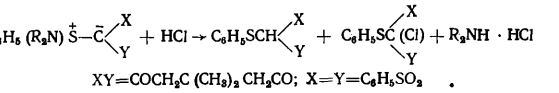


Y=$COOCH_3$ or CN; X=Cl, CF_3COO, NO_3, HSO_4, Br or $ClCH_2COO$.

However, the diphenyl-substituted trifluoroacetylbenzoylselenonium ylide is cleaved at the Se^+-C^- bond on treatment with HCl:[56]



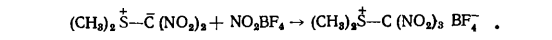
Dialkylarylaminosulphonium ylides react with HCl in an unusual manner, the S^+-N bond being ruptured and not S^+-C^-:[77]



XY=$COCH_2C(CH_3)_2CH_2CO$; X=Y=$C_6H_5SO_2$.

Thus the mode of cleavage of the DSY of Group VI elements by acids (and other strong electrophiles—see below) depends both on the nature of the carbanionic component and on the nature of the substituents at the onium atom. There is no doubt that the nature of the onium centre itself has an effect (cf. the cleavage of the tellurium ylides described above).

A single instance of the nitration of the DSY at the ylide carbon atom is known[130]:

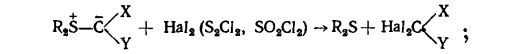


Treatment with N_2O_4 gives rise to tetranitromethane[130]. When the selenonium dinitromethylide is acted upon by nitronium fluoroborate, only tetranitromethane is formed[53].

It has been shown recently[73] that dimethylsulphonium diformylmethylide readily forms 1 : 1 adducts with certain inorganic salts, for example with ZnI_2.

(b) Reactions With Halogens and Other Halogenating Agents

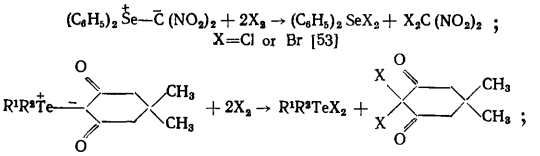
Under mild conditions, the ylide bond in doubly stabilised sulphonium dicyanomethylide[119] and dinitromethylide[126] is ruptured by halogens: Cl_2, Br_2, the mixed halogen BrCl, and their derivatives—S_2Cl_2 and SO_2Cl_2, which leads to diorganosulphides and dihalogenodinitromethanes or dihalogenomalononitriles:



X=Y=NO_2 [126] or CN [119] .

α-Chloromethyl sulphide, formed evidently on chlorination of the methyl group of the sulphide or the ylide, and a certain amount of side products, whose structure depends on the nature of the carbanionic fragment, have also been isolated from the reaction mixture. On the other hand, sulphonium dimethoxycarbonylmethylides are cleaved by halogens not only at the ylide bond but frequently also at the bonds linking other substituents to the onium sulphur[25]. The mode of these reactions depends on the nature of the organic substituents at the sulphur atom.

On treatment with halogens[53,127] or SO_2Cl_2 [53] in inert solvents, the selenonium[53] and telluronium[127] DSY yield the corresponding σ-chalcogenuranes:[53,127]

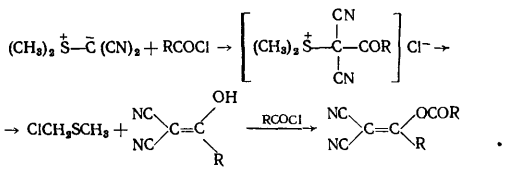


X=Cl, Br or I [127] .

Compounds with a "positive" halogen, namely *N*-chloro and *N*-bromosuccinimides, SO_2ClF, and others, react with sulphonium and selenonium dinitromethylides in an unusual manner[53,107,126]. Here the reaction products are the corresponding dihalogenodinitromethanes, i.e. the cleavage of the above dinitromethylide proceeds in such a way that the two "electrophilic" components of the reactant become linked to the carbanionic fragment, as happens in the interaction of DSY with HX (see above).

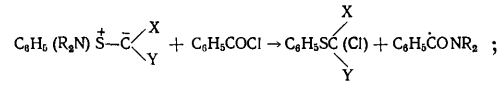
(c) Reactions With Acyl Chlorides

The interaction of the DSY of Group VI elements with acyl chlorides has been studied in a number of investigations[77,119,126,131] and it has been found that the sulphonium dinitromethylides do not react with carboxylic acid chlorides[126] while dicyanomethylides give rise to the dicyanovinyl ester of the carboxylic acid together with the salt $(CH_3)_2S^+-\bar{C}(CN)_2.2HCl$ and chloromethyl methyl sulphide[119]:



The interaction diorganosulphonium dimethoxycarbonylmethylides with acetyl chloride proceeds differently depending on the nature of the substituents at the sulphur atom[131]. Whereas the diphenyl derivative yields diphenyl sulphide (the second reaction product was not indicated), in the methylphenyl and benzylphenyl analogues the S^+–Alk bond is cleaved with formation of $C_6H_5SC(COCH_3)(COOCH_3)_2$ and alkyl chlorides.

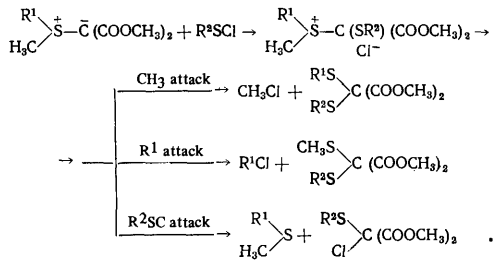
As in the reactions with HX, the S^+–N bond is ruptured in aryl(dialkylamino)sulphonium ylides[77]:



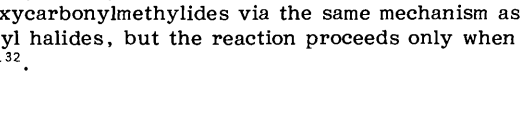
XY=$COCH_2C(CH_3)_2CH_2CO$; X=Y=$C_6H_5SO_2$.

(d) Interaction With Sulphenyl Halides and Sulphenyl Derivatives

The interaction of the ylides of Group VI elements with electrophiles of the type RSX (X = Cl or Br) has been studied in relation to a series of sulphonium[25,125,126] and selenonium[53] ylides. Under the influence of sulphonyl halides, sulphonium dimethoxycarbonylmethylides are initially sulphenated at the carbanionic centre and the resulting salt can be cleaved by the counterion X^- in three ways; the preferential occurrence of a particular reaction depends on the nature of the substituent at the sulphur atom and the nucleophilic properties of X^-:[25]



Electrophiles such as HBr and the halogens react via an analogous mechanism[25]. Sulphonium[125,126] and selenonium[53] dinitromethylides are converted into dinitrodi(phenylthio)-methane and the corresponding chalcogen dichlorides on treatment with benzenesulphenyl chloride. The cause of this effect of C_5H_5SCl is that the chalcogenonium salt formed in the first stage does not have sufficient time to be cleaved by the counterion Cl^- and is in fact cleaved by a second electrophile molecule at the M^+–C^- bond[53,126]:

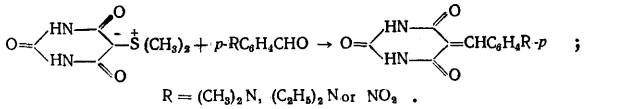


M=S or Se .

Sulphenyl thiocyanates RSSCN react with sulphonium dimethoxycarbonylmethylides via the same mechanism as sulphenyl halides, but the reaction proceeds only when R is an aryl[132].

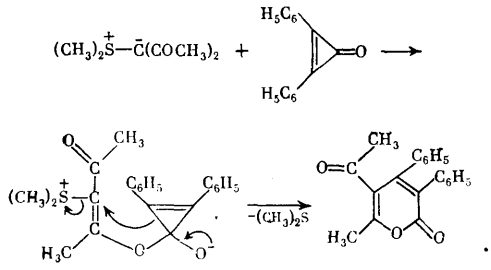
2. Interaction With Compounds Containing Multiple Bonds

Owing to the considerable delocalisation of the negative charge of the carbanion by the two electronegative substituents, the nucleophilic properties of the doubly stabilised chalcogenium ylides are weakened so much that, in contrast to the singly stabilised ylides, they do not usually interact with carbonyl compounds. In essence, there exists only one example of this reaction[133]:

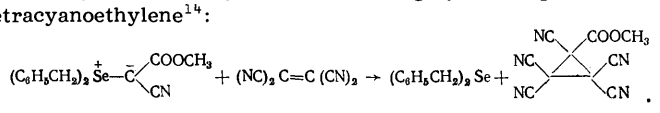


R = $(CH_3)_2N$, $(C_2H_5)_2N$ or NO_2 .

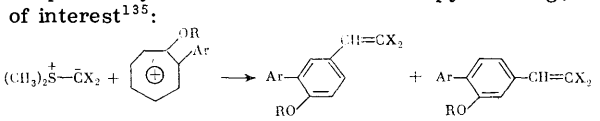
The reaction of the dimethylsulphonium ylide with the highly electrophilic diphenylcyclopropenone proceeds under extremely severe conditions and not via the classical mechanism, because the carbonyl group of the ketone is in fact preserved[134]:



The low nucleophilicity of the doubly stabilised chalcogenonium ylides is manifested by the fact that, in contrast to the singly stabilised ylides, which give rise to cyclopropanes on reaction with activated olefins (dibenzoylethylene, dimethyl fumarate, and acrylonitrile),[1,2] the DSY usually do not react with these compounds. However, substituted cyclopropanes have been obtained in high yields on reaction of dibenzylselenonium ylides with the highly electrophilic tetracyanoethylene[14]:

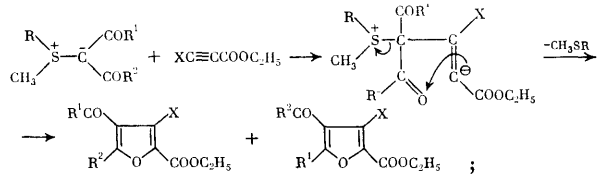


The fairly ready alkylation of dimethylsulphonium dicyano- and diethoxycarbonylmethylides by tropylium cations, which is accompanied by the contraction of the tropylium ring, is also of interest[135]:



The ratio of the reaction products depends on the nature of R and X. For example, the compound with X = CN gives rise exclusively to the isomer in which the dicyanovinyl group is in the *para*-position relative to the RO group.

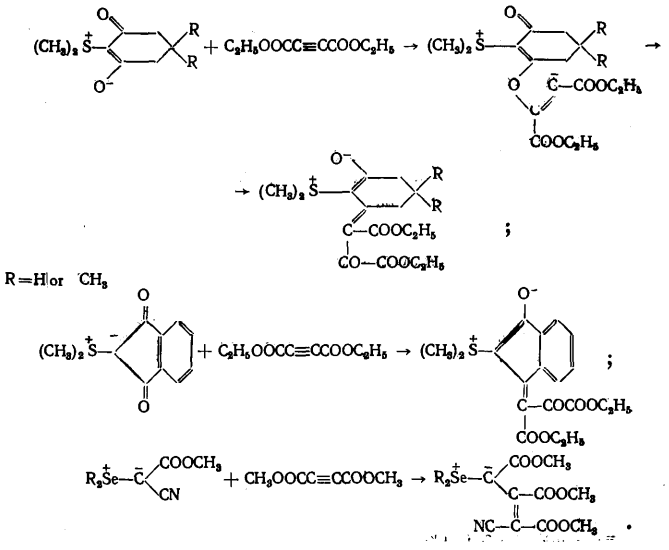
In contrast to compounds with a double bond, ethoxycarbonylacetylenes react with various sulphur[87,136] and selenium[120,121] DSY with at least one keto-group, the products being furans:



M=S [87, 136] or Se [120, 121]; R=CH_3 or C_6H_5;
R^1=Alk, C_6H_5 or OC_2H_5; R^2=Alk or C_6H_5;
X=H or $COOC_2H_5$.

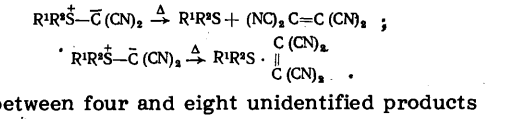
Ylides with two different keto-groups ($R^1 \neq R^2$) give rise to mixtures of two isomeric furans in different proportions, while keto(alkoxycarbonyl)sulphonium ylides ($R^1 = OC_2H_5$,

R^2 = Alk or C_6H_5) yield only one substituted furan—the alkoycarbonyl group is not involved in the cyclisation[87,136]. Cyclic sulphonium diketoylides derived from indandione and dimedone[87,136], as well as selenium ylides with substituents other than carbonyl groups at the carbanionic carbon, react with diethylacetylenedicarboxylate in an extremely unusual manner[14]:



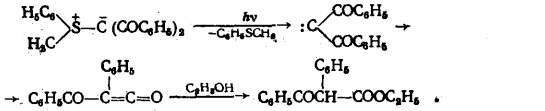
3. Thermolysis and Catalytic Decomposition of Ylides

Although the DSY of Group VI elements are highly stable with rare exceptions (certain selenonium nitroylides[53,107]) under the usual conditions, nevertheless at high temperatures they frequently decompose into diorganochalcogenides and the dimerisation products of the carbanionic fragment (thermolysis). Thus sulphonium dicyanomethylides[4,119] are cleaved, at temperatures exceeding by 30–50 °C their melting points, to give sulphides (if the latter are relatively volatile) and tetracyanoethylene[4,119]; if the sulphides are relatively involatile, charge-transfer complexes are formed between the sulphides and tetracyanoethylene[119]:

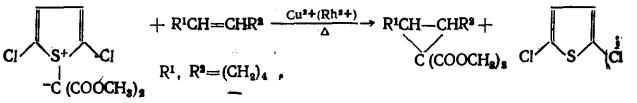


In addition, between four and eight unidentified products are also formed[4].

It has been suggested[119] that the thermolysis of the above ylides proceeds via a carbene formation stage. The possibility of the formation of carbenes on dissociation of the ylide linkage has also been indicated by data for the photolysis of a sulphonium dicarbonyl-stabilised ylide, since the product of the Wolff rearrangement was observed[137] (see also Trost[138]):

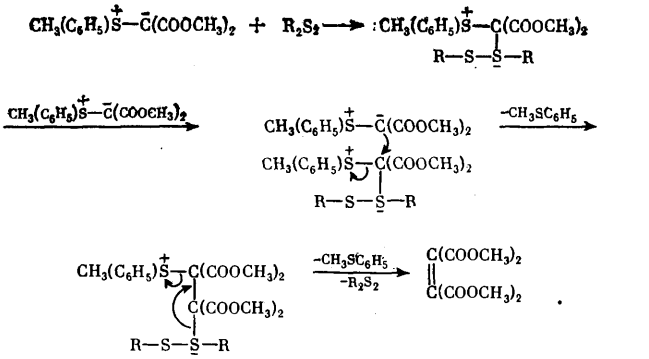


More significant evidence for the formation of carbenes on thermolysis of DSY is provided by the conversion of olefins into cyclopropane derivatives on treatment with 2,5-dichlorothiophenium dimethoxycarbonylmethylide in the presence of copper or rhodium catalysts[139]:

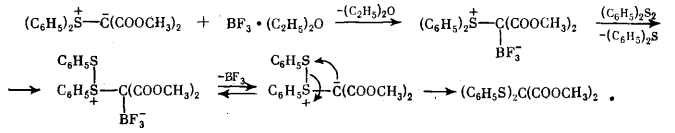


On interaction with activated (with respect to electrophilic substitution) aromatic compounds under analogous conditions, this ylide gives rise to products which are formally a result of the insertion of dimethoxycarbonylcarbene in a C–H bond of the aromatic ring[139,140].

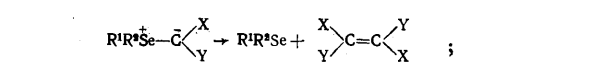
However, there is a possibility also of the catalytic decomposition of the DSY at the ylide linkage under milder conditions. Thus phenylmethylsulphonium dimethoxycarbonylmethylide readily decomposes at 35 °C into a sulphide and tetramethoxycarbonylethylene[141] in the presence of certain disulphides containing electron-accepting substituents: $(AlkO)_2S_2$,[142] $(C_6H_5CO)_2S_2$,[142] and $(CF_3)_2S_2$,[141] while on heating in the absence of a catalyst the ylide undergoes the Stevens rearrangement[20,21] (see below):



One should note that, in the presence of boron trifluoride etherate, the ylide indicated above reacts with disulphides which do not contain electron-accepting substituents at the sulphur atom (for example, with diphenyl disulphide) in a completely different manner[143]:



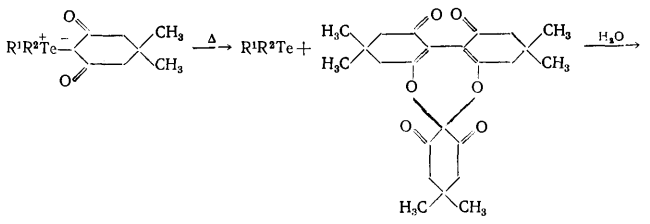
Different DSY readily decompose into the corresponding selenides and dimerisation products of the carbanionic fragment on treatment with catalytic amounts of tetramethylthiourea[144], thioamides[145], and episulphides[146]:



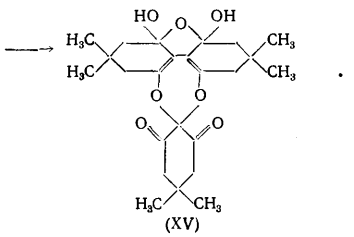
R^1=R^2=$C_6H_5CH_2$: X=CN, Y=$COOCH_3$ [144–146];
X=CN, Y=$COOC_2H_5$ [144] ;
R^1, R^2=$(CH_2)_4$: X=CN, Y=CN [144]/or $COOCH_3$ [144, 146].
R^1=R^2=CH_3: X=CN, Y=$COOCH_3$ [146] .

The mechanisms of all the above reactions involve the initial addition of the thio-derivatives to the ylide linkage with their subsequent elimination[144–146].

The anomalous course of the thermolytic reaction from the standpoint of the structure of the conversion product of the carbanionic fragment has been observed for diorganotelluriumdimedone ylides[147]. When these ylides were refluxed in *p*-xylene, the corresponding tellurides and a compound to which the structure of the trimerisation product (XV) of the carbanionic fragment was attributed from spectroscopic data, were isolated in almost quantitative yields. The reaction probably proceeds via a carbene mechanism and compound (XV) is evidently formed as a result of hydration (in the course of the reaction or on subsequent treatment of the reaction mixture) of the compound (XIV) formed initially:



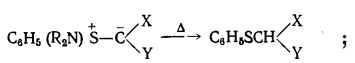
(XIV)



(XV)

Examples of this type of hydration are well known in the carbohydrate chemistry[148].

The unusual behaviour of dialkylaminoarylsulphonium ylides in different reactions has already been noted[77]. Their thermolysis, involving the rupture of the S^+–N bond and not the ylide linkage, also proceeds differently to the cases discussed above[77]:

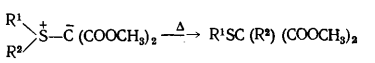


X, Y=$COCH_2C(CH_3)_2CH_2CO$; X=Y=$C_6H_5SO_2$.

4. Rearrangements

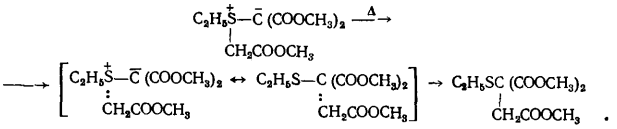
(a) The Stevens Rearrangement

One of the characteristic features of the sulphonium DSY is their ability to form products resulting from the migration of the corresponding groups from the sulphonium centre to the neighbouring carbanionic carbon atom[19,21]. The reaction proceeds under extremely severe conditions requiring heating (for 5–20 h) at 160–200 °C in sealed tubes:



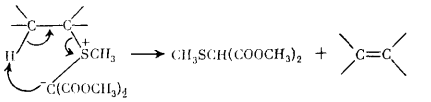
R^1=R^2=CH_3; R^1=C_6H_5, R^2=CH_3; R^1=CH_3, R^2=$C_6H_5CH_2$; R^1=C_2H_5, R^2=CH_3OCOCH_2 .

The observation of a CINP signal (in the region characteristic of methylene protons) on rearrangement of ethylmethoxycarbonylmethylenesulphonium methoxycarbonylmethylide[21] suggested that the reaction proceeds via the homolytic cleavage of the ylide with formation of an intermediate radical pair, which subsequently recombines to the rearrangement product:

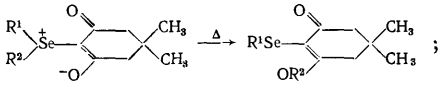


This mechanism has been confirmed by the finding that the groups capable of the resonance delocalisation of the unpaired electron ($C_6H_5\dot{C}H_2$, $\dot{C}H_2COOCH_3$) migrate most readily.

Alkylmethylsulphonium dimethoxycarbonylmethylides in which there is at least one hydrogen atom at the β-carbon atom of the alkyl groups (C_2H_5, n-C_4H_9, t-C_4H_9) undergo the Hofmann elimination on heating, leading to the formation of dimethylmethylthiomalonate and the corresponding olefins, and not the Stevens rearrangement[19,21]. This reaction probably proceeds via a five-membered cyclic transition state:

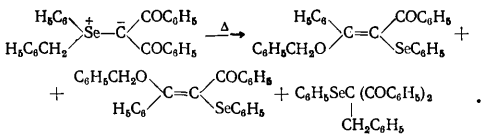


The migration of groups in selenonium diketoylides[149] and dimethylsulphonium formylmethylide[79] takes place differently. Under relatively mild conditions (refluxing in benzene or xylene) (compared with sulphonium ylides), the benzyl and phenyl groups in phenylbenzyl- and phenylmethyl-selenoniumdimedone ylides migrate to the oxygen atom (O-migration) and not the ylide carbon atom (Stevens rearrangement):

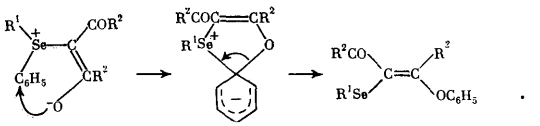


R^1=C_6H_5, R^2=$CH_2C_6H_5$; R^1=CH_3, R^2=C_6H_5; R^1=R^2=C_6H_5 .

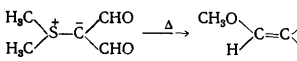
In the rearrangement of methylphenylselenonium dibenzoyl methylide (the phenyl group migrates) and diphenylselenonium benzoylmethylide O-migration also takes place and the C-migration product (Stevens rearrangements) is formed only in the case of phenylbenzylselenonium dibenzoylmethylide together with the products of the O-migration of the benzyl group (a mixture of the benzyl ethers of the *cis*- and *trans*-enols of 1,3-diphenyl-2-phenylselenopropane-1,3-dione):[149]



It is believed[149] that the rearrangement of the phenylbenzylselenonium ylides proceeds via a mechanism similar to that for the sulphur ylides, while the migration of the phenyl group in methylphenyl- and diphenylselenonium ylides proceeds via a mechanism involving intramolecular nucleophilic substitution in the benzene ring:



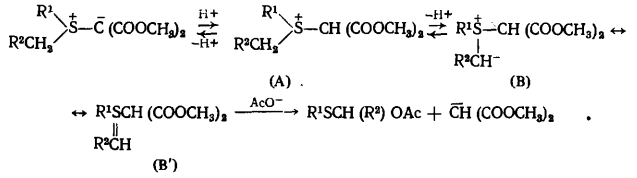
The O-migration in dimethylsulphonium diformylmethylide takes place under very severe conditions[79]:



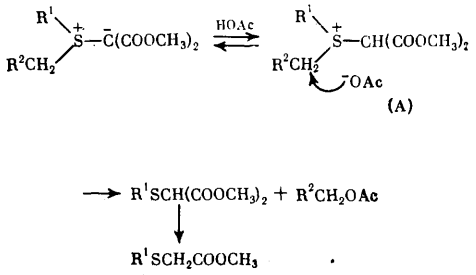
It should be noted yet again that tellurium-containing dimedone ylides undergo only thermolysis on heating regardless of the nature of the substituents at the tellurium atom[147].

(b) The Pummerer Rearrangement

The similarity of the structures of the ylides and sulphoxides containing the semipolar S^+-C^- and S^+-O^- bond suggests the similarity of the chemical properties and in particular the ability of ylides to undergo the Pummerer rearrangement. Indeed sulphonium dimethoxycarbonylmethylides containing sufficiently acidic methylene groups (R^2 = COOR) undergo the Pummerer rearrangement on heating with acetic acid, giving rise to alkoxycarbonyl (alkylthio)methyl acetates and dimethyl malonate[23]. In the presence of acids the ylides are in equilibrium with sulphonium salts A and the less stable but more nucleophilic than the initial compounds ylides (B and B'), nucleophilic attack on which by the acetate ion leads to the final products:

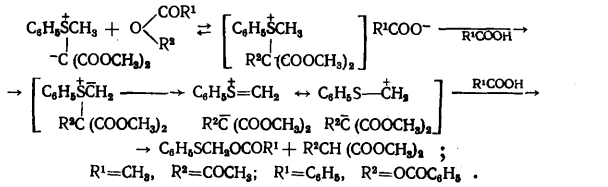


Ylides with less acidic CH_2 groups (R^1, R^2 = Alk or Ph) do not give rise to the products of the Pummerer reaction on heating in acetic acid, forming instead methoxycarbonylmethyl sulphide and alkyl acetates[23]:

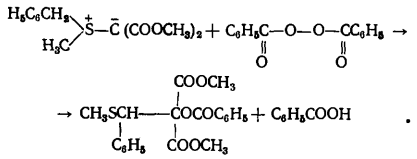


The cause of this mode of reaction is the weaker acidity of the CH_2 groups in the initial ylides, which reduces sharply the concentration of the nucleophilic ylides (B) and drives the reaction via the pathway involving nucleophilic substitution in the sulphonium salt (A), which is present in large amounts. It has been shown[23] that the mode of the Pummerer or substitution reactions depends on the strength of the acids employed: in strong acids (CF_3COOH and $CHCl_2COOH$) ylides of the first type (with alkoxycarbonyl substituents at the onium sulphur atom) undergo the substitution reaction, while in acids weaker than acetic (CH_3CH_2COOH) ylides of the second type can undergo the Pummerer rearrangement together with substitution.

The Pummerer rearrangements have been investigated[150,151] for arylmethylsulphonium dimethoxycarbonylmethylides in the presence of acetic anhydride and benzoyl peroxide. These reactions involve the initial formation of a sulphonium salt as a result of nucleophilic attack on the ylide carbanion, the deprotonation of the salt, the heterolysis of the S^+-C^- bond (rate-determining stage), and the interaction of the intermediate formed with the anion[150,151]:

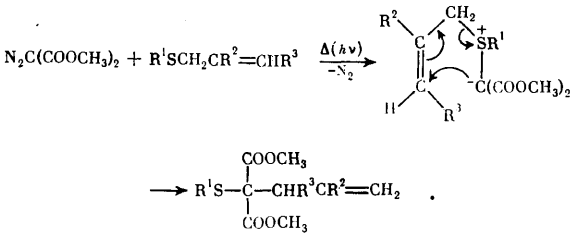


We may note that, in contrast to its methylphenylsulphonium analogue, benzylmethylsulphonium dimethoxycarbonylmethylide undergoes an unusual rearrangement in the presence of benzoyl peroxide via the following mechanism[151]:

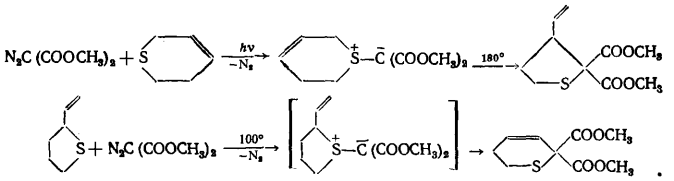


(c) The Allyl Rearrangement

A characteristic feature of doubly stabilised ylides—the intermediates formed in the thermal and photochemical interaction of carbenes and allyl sulphides—is their ability to undergo the allyl rearrangement, from the products of which one in fact infers the intermediate formation of the ylides[32-34]:



This mechanism has been confirmed by the isolation of a stable ylide derived from a cyclic allyl sulphide and its subsequent allyl rearrangement under other conditions[32,35]:

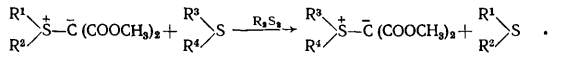


5. Transylidation

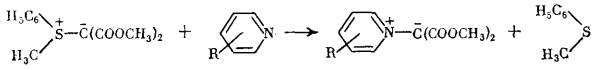
Transylidation is a reaction in which one onium group in ylides is replaced by another. Such reactions are influenced significantly by the nature of the onium group in the ylide and of the element in the reagent, the nature of the substituents at the ylide carbon atom, and the reaction conditions (solvent and catalyst).

The influence of various factors on the transylidation of sulphonium ylides by sulphides and pyridine has been studied in detail[141,142]. In the presence of catalytic amounts of

certain disulphides, methylphenylsulphonium dimethoxycarbonylmethylide undergoes smooth transylidation with various sulphides:



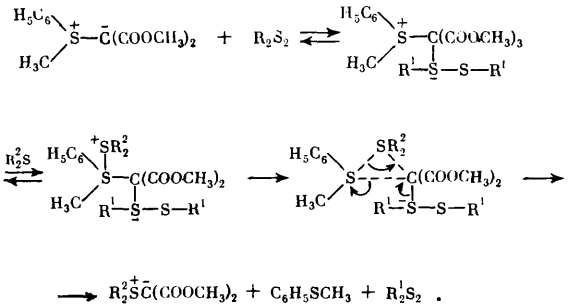
In the absence of a catalyst, the transylidation of the methylphenylsulphonium ylide with dimethyl sulphide (present in a 15-fold excess) proceeds very slowly and does not go to completion. On the other hand, in the presence of a catalyst the transylidation of alkylphenylsulphonium ylides and dialkyl sulphides proceeds readily, that of dialkyl ylides with dialkyl sulphides is much more difficult, and that of dialkylsulphonium ylides with alkyl phenyl sulphides (and probably diphenyl sulphides) hardly occur at all[142]. In other words, as the nucleophilic properties of the sulphides are reduced (Alk_2S < AlkSPh < Ph_2S), their ability to effect transylidation is sharply diminished. The marked influence of the nucleophilic properties of the organoelemental component on transylidation also follows from the results of a study of the reaction of methylphenylsulphonium dimethoxycarbonylmethylide with pyridine and its derivatives[142]:



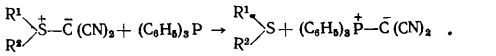
Whereas the yields of the pyridinium ylides in the reaction with 3- and 4-picolines and pyridine are 96–100%, the yield of the reaction with the weakly basic 4-cyanopyridine is only 7%.

The nature of the electronegative substituents at the carbanionic carbon plays a significant role in transylidation. The more nucleophilic the ylide carbon, the greater the ease of the transylidation. Diketoylides, for which the contribution of the betaine structure is relatively important, are transylidated to a much smaller extent than dimethoxycarbonylmethylides with a more nucleophilic carbanionic carbon (owing to the smaller contribution of betaine structures). One should also note that the yields of ylides also depend on their resistance to thermolysis. Indeed, in the reaction of dimethylsulphonium dicyanomethylide with diethyl sulphide, a new ylide was not detected, while the yield of dimethyl sulphide was 95%.

The above transylidation reactions proceed fairly readily only in the presence of catalysts—disulphides with powerful electron-accepting substituents at the sulphur atom (OR, C_6H_5CO, C≡N,[142] and CF_3 [141]). The authors[141,142] therefore proposed the following catalytic mechanism of the transylidation reaction: as a result of the nucleophilic attack on the electron-deficient sulphur atom of the disulphide by the ylide carbon atom, an unstable intermediate complex is formed. Nucleophilic attack on this complex by the sulphide or pyridine leads to a trimolecular complex, which then decomposes to the final ylide and a disulphide[142]:

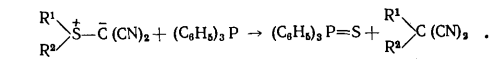


The influence of external conditions (solvent and catalyst) on transylidation can be illustrated by the reaction[152]:

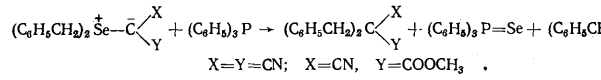


This reaction proceeds neither in benzene, nor in carbon tetrachloride, nor in acetic acid. Only in the presence of a catalyst (BF_3) in acetic acid does transylidation take place fairly readily[152].

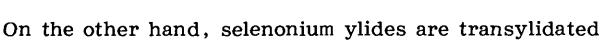
In many instances transylidation is accompanied by side reactions—transalkylation and dechalcogenation. Thus, when sulphonium cyanomethylides interact with triphenylphosphine, the products of the competing desulphuration of the ylide, mainly triphenylphosphine sulphide and dialkylmalononitriles, are formed together with triphenylphosphonium dicyanomethylide and sulphides[153–155]:



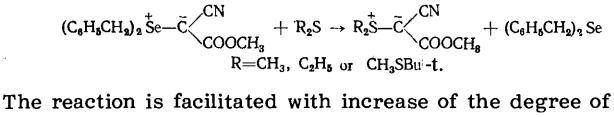
In certain cases dechalcogenation is the main pathway in the reaction between ylides and organoelemental compounds. In the reaction of dibenzylselenonium ylides containing two electron-accepting substituents with triphenylphosphine in CH_2Cl_2 mainly triphenylphosphine selenide is formed together with the products of the alkylation of the carbanionic fragment and a small amount of dibenzyl diselenide[156]:



It is noteworthy that mainly the usual transylidation takes place in the reaction between dibenzylselenonium *N*-tosylimide and triphenylphosphine[156]:

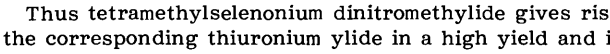


On the other hand, selenonium ylides are transylidated with sulphides, but only in the presence of CS_2, and do not form transalkylation products at all[157]:



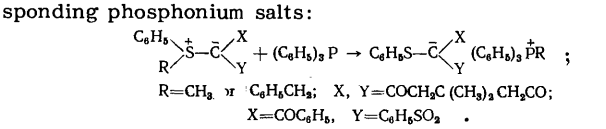
The reaction is facilitated with increase of the degree of branching of the substituent in the sulphide.

The influence of the substituents at the ylide heteroatom can be followed in relation to the interaction of selenonium dinitromethylides with thiourea[107]:



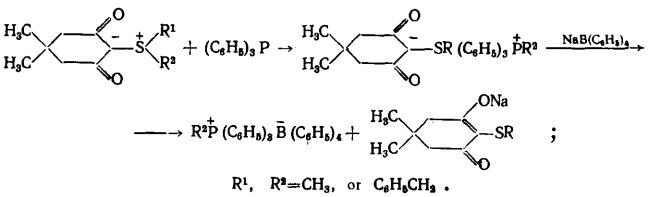
Thus tetramethylselenonium dinitromethylide gives rise to the corresponding thiuronium ylide in a high yield and in the absence of a catalyst. For R = $C_6H_5CH_2$, a 1 : 1 complex with thiourea is formed, while for R = C_6H_5 the reaction does not occur at all.

In the study of the interaction of sulphonium ylides derived from dimedone and phenylsulphonylacetophenone with triphenylphosphine a third possible pathway in the reaction of ylides with organoelemental compounds was discovered[157,158]. This reaction, which can be regarded as partial dealkylation of sulphonium ylides, leads to the formation of the corresponding phosphonium salts:



In the interaction of dialkylsulphonium dimedone ylides with triphenylphosphine the phosphonium salts could not be isolated probably as a consequence of their lability, but their

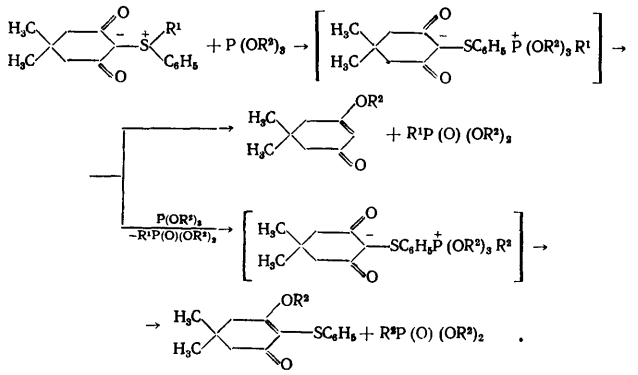
formation was demonstrated by carrying out the reaction in the presence of sodium tetraphenylborate:



R^1, R^2=CH_3, or $C_6H_5CH_2$.

Tris(dimethylamino)phosphine reacts similarly with sulphur-containing DSY.[159,160]

The reactions of sulphonium diketoylides with trialkyl phosphites take place via the intermediate formation of quasi-phosphonium salts and lead ultimately to alkyl phosphinates and 3-alkoxy-2-benzenesulphenyl-5,5-dimethylcyclohex-2-enone:[161]

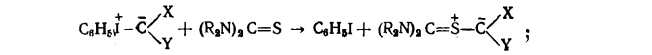


This reaction is a new example of the non-classical Arbuzov rearrangement.

Thus the transylidation reaction can be regarded as a special case of the interaction of the DSY of Group VI elements with organoelemental compounds.

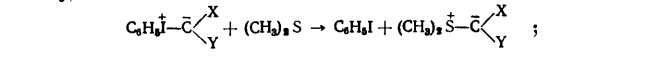
The transylidation reactions examined above are of interest from the standpoint of the chemical properties of ylides, but have not found fairly wide synthetic applications. It is evident, however, that the transylidation of relatively readily available aryliodonium ylides can find applications in the synthesis of certain types of chalcogenium ylides.

For example, thiuronium ylides, which are otherwise difficult to obtain, can be synthesised readily and in the absence of a catalyst[9,162,163]:



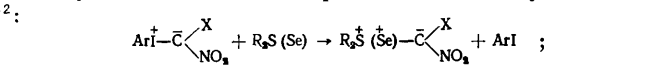
X, Y=$COCH_2C(CH_3)_2CH_2CO$ [163]; X=Y=NO_2 [9] .

Various dimethylsulphonium ylides derived from β-dicarbonyl compounds have been obtained via iodonium ylides in the presence of copper salts[115-118] and toluene-*p*-sulphonic acid[164] as catalysts:



X=Y=$COCH_3$ [115], COC_6H_5 [116]; X=$COCH_3$, Y=$COOC_2H_5$ [117]; XY=$COCH_2C(CH_3)_2CH_2CO$ [118], $COOC(CH_3)_2OCO$ [164] .

Furthermore, iodonium nitromethylides can serve as reagents for the synthesis of various sulphur and selenium ylides[9,107,162]:

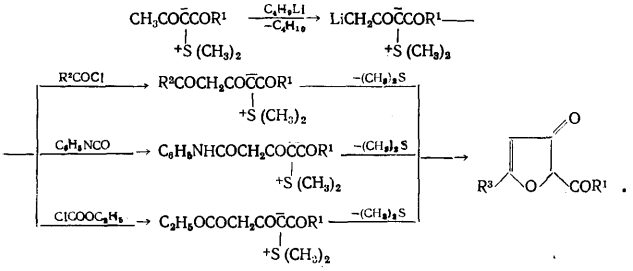


Ar=C_6H_5, or *p*-$O_2NC_6H_4$; X=$COOCH_3$, COC_6H_5, or NO_2; R=CH_3, n-C_4H_9, $C_6H_5CH_2$, or R_2=$(CH_2)_4$.

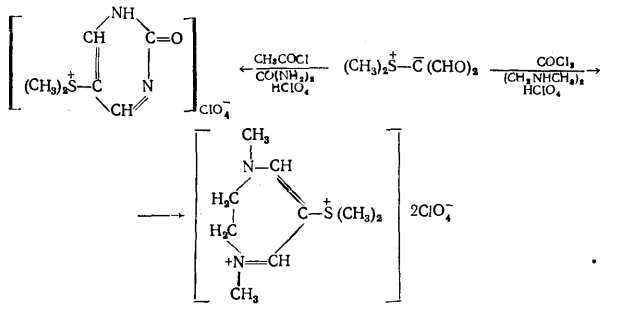
It is noteworthy that diphenyl chalcogenides do not enter into this reaction.

6. Other Reactions of the DSY

The reactions discussed above (with the exception of salt formation and the interaction of certain types of DSY with compounds containing multiple bonds) proceed with dissociation of the M^+–C bond. New reactions of the DSY, in which the groups linked to the onium atom are transformed without the dissociation of the M^+–C bonds, have been discovered recently. Thus at temperatures from −10° to −15 °C various sulphonium diacetylmethylides are readily substituted by lithium in the methyl group of the acetyl residue by reaction with butyl-lithium or lithium isopropylamide in THF, giving rise to monolithio-derivatives[165,166]. Treatment of these compounds with various reagents leads to new sulphur DSY; some of these compounds readily cyclise to furans[165,166]:



Certain heterocyclic compounds can be obtained from dimethylsulphonium diformylmethylide[79]:



After the manuscript had been sent to the editors, a number of studies on doubly stabilised sulphur and selenium ylides were published[167-179]. Condensation of dimethyl sulphoxide with methanedisulphonyl fluoride yielded a new type of sulphur ylides with two sulphonyl fluoride groups at the ylide carbon atom[167]. An unusual method of synthesis of aminosulphonium methylides by the interaction of arenesulphinic acids with active methylene compounds has been developed[168] and it has also been shown that these ylides undergo a Stevens type rearrangement[168]. The reaction of dicarbonyl-stabilised sulphonium ylides with sulphides[169] and the synthesis of thioxanthenium ylides and their base-catalysed rearrangement[170] have been studied and yet another example of the synthesis of a sulphur ylide from an iodonium ylide has been described[171]. The onium structure of doubly stabilised chalcogenonium ylides with complete delocalisation of the negative charge over the carbanionic fragment and with a single bond between the sulphur and the ylide carbon has been confirmed in relation to sulphonium dinitromethylides by X-ray diffraction, by the dipole moment method, and by quantum-chemical calculations[172]. Polarographic oxidation of sulphur-containing nitromethylides proceeds with abstraction of a single electron from the carbanionic fragment

and the formation of the corresponding radical-cations[173]. In the polarographic reduction of dicarbonyl-stabilised selenium ylides the bond between selenium and the ylide carbon atom undergoes two-electron cleavage with formation of a selenide and a dicarbonyl compound[174]. Analogous products are obtained in the chemical reduction of selenium ylides by mercaptans and mercaptoacids[175]. Thermolysis of selenonium ylides based on dimedone and indan-1,3-dione in the presence of copper sulphate proceeds via the corresponding carbenes, judging from the reaction products[176]. The unusual class of doubly stabilised sulphur and selenium ylides with the onium group at the carbanionic carbon atom, namely ylide salts, has begun to be studied systematically in recent times[177-179]. Their synthesis by the reaction of sulphoxides and selenoxides with phosphonium and sulphonium salts containing an active methylene group[177], their protonation, their cleavage by acids[178], and their rearrangements[179] have been described. Ylide salts are cleaved by hydrogen chloride with reformation of the initial active methylene compounds and dichloroselenide[178], i.e. via the same mechanism as sulphur- and selenium-containing dinitromethylides and doubly stabilised tellurium ylides and in this respect they differ from the vast majority of the chalcogenonium ylides.

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The Structure and the Electron-donating Properties of Tertiary Arsine Oxides

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The complex-forming and physicochemical properties of tertiary arsine oxides are analysed in connection with the significant differences between them and the closest organophosphorus analogues. Attention is focused on the reactivities of organoarsenic ligands in complex-formation reactions with acids and metal salts. The specific features of the steric and electronic structures of arsine oxides and the mechanism of the transmission of the influences from groups via the arsenic atom to the reaction centre (the arsenyl oxygen) are discussed. Heterophase reactions in the extraction of acids and salts are considered within the framework of a single model of donor-acceptor processes in solution.
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I. INTRODUCTION

The chemistry of organoarsenic compounds (OAC) is now going through a period of new advance due to the appearance of realistic prospects for the practical utilisation of these derivatives in various branches of science and technology. At the same time, the development of this field is held back by the lack of review publications dealing with the numerous but extremely varied studies on the characteristics of the behaviour of the OAC in many important chemical reactions. This applies fully to the study of the properties of tertiary arsine oxides R_3AsO in reactions of the electron donor–electron acceptor (EDA) type in which the molecular complexes of R_3AsO with organic and inorganic Brønstedt and Lewis acids are formed. Such reactions constitute the basis of the complex formation processes in the homogeneous solutions and heterophase systems, where R_3AsO behave as strong ligands of the neutral type.

This valuable property of R_3AsO has for a long time attracted the attention of specialists in the field of coordination chemistry, who believe that the central problem is the search for relations between the electronic and steric structures of the substituents R at the arsenic atom and the reactivity of the R_3AsO in processes of the EDA type. The extensive experimental data accumulated hitherto have not so far been surveyed and arranged systematically, which limited the application of these compounds in complex formation and extraction processes. This review fills this gap and is devoted to the latest advances in the theory of the structure of the OAC and the applications of tertiary arsine oxides and ligands in the formation of EDA complexes.

Numerous methods of synthesising compounds of tetracoordinate arsenic have been described in detail in specialist publications and monographs[1-60].

II. THE ELECTRONIC STRUCTURE OF ORGANOARSENIC MOLECULES

The Group VB elements—nitrogen, phosphorus, arsenic, antimony, and bismuth—have similar structures of the outer electron shells, consisting of two *s* and three *p* levels. In tervalent compounds of these elements ER_3 three *p* bonds of the heteroatoms E with the groups R should therefore be at 90° angles relative to one another and the free electron pair should be of the pure *s* type. In reality the 2*s* orbital of the electron pair in nitrogen compounds is hybridised with the 2p orbitals, which leads to the formation of four equivalent hybrid sp^3 orbitals. For other Group VB elements, the hybridisation of the *s* and *p* levels is not observed, while the R–As–R valence angles are in the range from 91.8° in AsH_3 to 101° in AsF_3 and AsI_3 (for the majority of the derivatives, the angle is 96°)[61]. The valence angle hardly changes on oxidation of tertiary arsines to arsine oxides, i.e. on passing to the tetracoordinate state $R_3As^+-O^-$.[62]

One of the popular models of the arsenyl group involves the cooperative interaction between the arsenic and the oxygen in the $\geq As^+-O^-$ σ-bond and the $p_\pi-d_\pi$ conjugation of the unshared electron pairs of oxygen with the highest vacant 4*d* orbitals of arsenic. As a result of this, the $\geq As\ldots O$ bond acquires partial double bond character depending on the extent of the $p_\pi-d_\pi$ conjugation. This model has been confirmed in the study of the dipole moments of arsenyl compounds[63-65].

The study of a number of oxo-bases R_3NO, R_3PO, and R_3AsO ($R=C_8H_{17}$) by X-ray electron spectroscopy showed that[66] the spectra of R_3NO and R_3AsO are similar, while the spectrum of R_3PO differs significantly as a consequence of the $p_\pi-d_\pi$ interaction of the oxygen in the phosphoryl group with the 3*d* orbitals of the phosphorus atom. This permits the conclusion that, if the $p_\pi-d_\pi$ interaction actually occurs in the arsenyl group, its extent is small and at any rate significantly smaller than in phosphorus compounds. Comparison of the reactivities of compounds of the above series in the formation of charge-transfer complexes with molecular iodine in inert solvents leads to the same conclusion[67]. In this case the reaction constants, the interaction energy, and the degree of charge transfer are similar for R_3NO and R_3AsO, while the corresponding quantities for R_3PO are appreciably smaller.

In order to resolve this contradiction, most varied physicochemical methods, such as ^1H and ^{19}F nuclear resonance[68-71] ^{75}As [72-74] and ^{35}Cl [75] nuclear quadrupole resonance, photoelectron X-ray spectroscopy[76], and electron and vibrational

spectroscopy[77-80] have been used. However, unambiguous conclusions cannot be reached owing to the evident discrepancies between the results obtained by different methods. The solution of this problem was hindered also by the lack of reliable bond lengths and valence angles in arsenic compounds, which were determined accurately only very recently[81-84].

The first mention of the vibrational frequency of the arsenyl group was made in a study[85] where intense absorption maxima in the infrared spectra of tertiary arsine oxides (TAO) at 815 and 844 cm^{-1} were assigned to the AsO groups. The intense absorption bands in the range 815–910 cm^{-1} have also been assigned[86-89] to the As–O linkages. Having studied the infrared spectra of compounds of the type Ph_3MX (M = P, As, or Sb; X = O, Se, or S) in the range 400–3000 cm^{-1}, Jensen and Nielsen[90] determined the absorption frequencies of the As = O (881 cm^{-1}) of $Ph–As_{(as)}$ (474–479 cm^{-1}) groups. The infrared spectra of organoarsenic ligands (L) and complexes of the type ML_2X_2 (L = Ph_3AsO or Ph_2MeAsO; X = Cl or Br; M = bivalent metals ranging from Mn to Zn) have been investigated and discussed[91]. Having discovered that the stretching vibration frequencies ν(As–O) occur in the range 840–910 cm^{-1}, the authors[91] determined them experimentally in the range from 855 to 910 cm^{-1}. The earlier assignments of the intense absorption band in the spectra of triphenylarsine oxide[86-88,92] were confirmed in a study[93] of iso-substituted compounds.

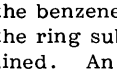
Deacon and Green[94] synthesised and investigated by infrared spectroscopy in the range 200–1650 cm^{-1} the complexes of triphenylarsine oxide with zinc, manganese, cobalt, and mercury ions (saturated solutions in chloroform) and obtained a satisfactory agreement with the results of other studies[90-93]. The absorption maximum at approximately 880 cm^{-1}, assigned to the stretching vibrations of the AsO bond, is resolved into a doublet with frequencies of 885 and 877 cm^{-1} in the spectrum of the solid specimen. A special method for the synthesis of virtually anhydrous complexes made it possible to isolate preparations giving rise to a weak peak in the region of 3300 cm^{-1}; the water absorption bands in the range 200–1650 cm^{-1} are entirely absent.

The infrared spectra of a large number of aromatic and aliphatic derivatives of tetracoordinate arsenic have been published[95]. All the spectra have been interpreted qualitatively and the influence of the vibrations of the benzene ring, the substituents at the arsenic atom, and the ring substituents on the ν(AsO) absorption bands was examined. An equation relating the stretching vibration frequencies of the M = X bonds to the bond order was derived for molecules of the type $R_3M–X$ (where R = alkyl: M = P, As, or Sb; X = O, S, Se or Te), taking into account the molecular masses[96]. The force constants and bond orders have been calculated from the Raman and infrared spectra of the compounds $(CH_3)_3MO$ (where M = N, P, or As). According to the authors[95], there is extensive $p_\pi–d_\pi$ interaction, which is particularly characteristic of the phosphorus and arsenic compounds[97], while according to other data[98], the extent of the interaction is small.

It is noteworthy that many studies on the vibrational spectroscopy of organic compounds of arsenic are to a large extent descriptive and in only some of them has an attempt been made to relate the spectroscopic data to the structures and properties of the compounds. Such comparisons were made for the first time in a number of investigations[77,79,99-102], whose authors were able to determine experimentally the characteristic spectroscopic features of the arsenyl group, to measure its vibrational frequencies for the class of compounds investigated, to find the relation between ν(AsO) and the nature of the substituents at the arsenic atom, and to investigate the influence of solvents on ν(AsO). However, the study of the vibrational frequencies does not yield complete information about the molecular structure. The characteristics of the structure of the electron shell are manifested most completely in the intensities (A) and polarisation of the spectral lines and bands.

The integral stretching vibration band intensity of the arsenyl group $A_{As=O}$ was first calculated[93] for triphenylarsine oxide. Subsequent careful determination of the $A_{As=O}$ for different TAO showed that the band has a high intensity comparable to the integral intensities of the bands due to the phosphoryl and carbonyl groups[100-102]. It has been noted[100] that, on passing from tertiary arsine oxides to arsonic acid esters, the integral intensity of the absorption band diminishes. This indicates an increase in the multiplicity and the strengthening of the AsO bond in the esters.

Hypotheses concerning the fractional AsO bond order in TAO have been put forward in several investigations. Thus, having calculated the force constants and the stretching vibration frequencies of the As–O and As = O bonds (770 and 964 cm^{-1} respectively), an experimental stretching vibration frequency of approximately 880 cm^{-1} was obtained on the basis of the study of the vibrational spectra[91,103]. The AsO bond order calculated from the formulae of Gordy and Siebert proved to be 1.5.[97] In the calculation of the stretching vibration frequency, Shagidullin et al.[99] introduced a correction for the ionic shortening of the bond. The experimental AsO bond length in Ph_3AsO is 1.66 Å,[104] which is intermediate between the values calculated from the Shomaker–Stevenson formula for single and double bonds (1.74 and 1.58 Å respectively). The authors[104] also suggested that the multiplicity of the AsO bond can change under the influence of the electronic properties of substituents by virtue of the polarisation of the $d_\pi–p_\pi$ linkage. On the basis of the equation relating the stretching vibration frequency of the AsO bond to the overall electronegativity of the substituent R at the arsenic atom, it has been concluded that the bond under consideration is more polar than the PO bond[104].

On the basis of calculations of the parameters of the correlation of the stretching vibration frequency shift and the known reaction constants of the substituents and taking into account data indicating that the ν(As = O) vibrations are highly characteristic, Shagidullin and Lamanova[100] concluded that the substituent X is conjugated with the As = O group in the chain X—  —As = O. Since the conjugation has a significant influence on the parameters of the electronic transitions in molecules, such effects should be manifested in the ultraviolet spectra of the test compounds. There are no systematic literature data of this kind and it is only known that the unshared electron pair of the central atom in the phenyl derivatives of Group VB element interacts weakly with the π orbitals of the benzene ring[105-107], and, when the central atom does not have such electrons, there is no resonance interaction at all[108].

The overall electronic effect of the arsenyl groups is electronegative and in aromatic derivatives they behave as *meta*-directing substituents[69,109], i.e. as electron acceptors in relation to the benzene ring. If account is taken of the fact that the electronegativity of the arsenic atom is lower than that of the carbon atom (2.10 and 2.60 according to Pauling[110]), then the most acceptable hypothesis which will explain the above effect may be that of $p_\pi–d_\pi$ conjugation. Furthermore, it has been found that[69,109], the shifts of the p absorption band caused by substituents in the series of arsines and their oxides are analogous to the shifts for the corresponding derivatives of aromatic ketones. Since the keto-group is a typical *meta*-directing substituent, the results can be regarded as additional confirmation of the above hypothesis.

Comparison of the frequencies $\nu(As=O)$ with the additivity constants of the substituting groups obtained for organophosphorus compounds showed[111,112] that a linear relation between $\nu(As=O)$ and $\Sigma\chi$ (where χ is the constant of the phosphoryl shift) holds also for organoarsenic derivatives within the limits investigated. This confirms the analogy, noted previously, between the structures and properties of phosphorus and arsenic and also shows that the interactions of the PO and AsO bonds of the substituents are of the same type. The σ constants of arsenic-containing substituents can be found in Lobanov's thesis[113] and in all cases where substituents exhibit electron-accepting properties.

However, despite the fact that the amount of information which can be used for theoretical and semiempirical descriptions of compounds of the type R_3AsO is considerable[114], it is still insufficient for an unambiguous solution of the problem of the multiplicity of the As=O bond in organic compounds of arsenic. In conclusion of the discussion of the results of studies on the electronic structure of compounds of tetracoordinate arsenic, we may note that many most important problems in the chemistry of arsenic have still not been solved. Thus there have been virtually no quantum-mechanical calculations on the structures of arsenic compounds and the amount of double bond character in the arsinyl group and its dependence on the nature of the substituents at the arsenic atom has not been finally established, there are few data on the transmission properties of arsenic in different valence states, and the amount of information on its stereochemistry is insufficient[115-123]. The lack of these data complicates the specific synthesis of new organoarsenic preparations and retards their introduction into various branches of science and technology. In this connection one may hope that, as the theory of the structure of arsenic compounds develops, new fields of practical applications of this interesting class of organoelemental derivatives will be discovered.

III. THE BASICITY OF ARSENIC-CONTAINING EXTRACTANTS IN AQUEOUS AND NON-AQUEOUS SOLUTIONS

The adducts of tertiary arsine oxides with protic acids have been known for a long time. Stable complexes with nitric acid[124,125], chloroacetic acids[126,127], perchloric acid[128], and hydrogen halides[126,128] have been described. The first data concerning the basicity of TAO were obtained in 1941, when Nylen[129] determined the acid dissociation constants of the conjugate acids of trimethylarsine oxide ($pK_a=3.75$) and triethylarsine oxide ($pK_a=3.71$) in water at 20 °C. A wider set of TAO was investigated by Chernokal'skii et al.[130], who determined the basicities of a series of *para*-substituted aryldiethylarsine oxides having the general formula $p\text{-}XC_6H_4As(O)(C_2H_5)_2$ with a variable electronic structure of the substituent X. It was noted that all the TAO investigated are weak bases in water and that their basicity depends on the structure of the Group X. While the length of the hydrocarbon chains of the groups X has almost no influence on the basicity, there is a linear relation between the pK_a of the TAO and the Hammett constants. Analysis of the relations obtained enabled the authors to conclude that the tetracoordinate arsenic atom is capable of transmitting inductive and resonance effects but is a weaker conductor than carbon.

In order to refine the relations between the nucleophilicity of trialkylarsine oxides and their basicity, the pK_a of a series of TAO were determined in water[131]. It was found that oxides of the type Alk_3AsO are moderately strong bases in aqueous solutions, their thermodynamic protonation constants pK_a^T being in the range 3.59–4.03 depending on the structure of the alkyl groups. The lengths of the hydrocarbon groups in the range from $Alk=CH_3$ to $Alk=C_4H_9$ has almost no influence on the basicity, while their steric structure does have an influence. Using a series of oxides of *para*-substituted 10-aryl-5,10-dihydrophenarsazines, the influence of substituents in the *para*-position of the benzene ring on the basicity of the arsinyl oxygen was investigated[132] with the aid of $\sigma\rho$ analysis. The test oxides proved to be fairly weak bases, as shown by the absence of a sharp potential jump at the neutralisation point, with low values of pK_a^T even on titration in aqueous alcoholic media. The observed low reaction constant ρ confirms the earlier conclusion[130] that the electronic conductivity of arsenic is smaller than that of the elements in the Second Period. However, the data[132] concerning the relation between the structure of the compounds and their basicity cannot be regarded as correct for a number of reasons, the principal of which are the low basicity of the majority of the TAO in aqueous solutions, the inadequate accuracy of the measurement of pK_a^T under these conditions, and the short range of variation of ΔpK_a^T as the structure of the groups attached to arsenic is varied. The study of the basicity of the TAO in differentiating organic solvents, among which nitromethane and acetic anhydride are outstanding, is much more promising from this point of view[133].

In the study of the acid–base properties of organoelemental bases in non-aqueous media, the high basicity of the TAO in nitromethane and acetonitrile was noted[134,135]. These observations were fully confirmed in the determination of the basicity ($pK_{B,HX}$) of the oxo-bases in acetic anhydride by the spectrophotometric method and on comparing their electron-donating capacities in the formation of intermolecular hydrogen bonds with thiocyanic acid, deuterophenol, methanol, indole, methylaniline, and phenylacetylene[136]. The results show that triphenylarsine oxide (TPAO) becomes a fairly strong base on non-aqueous solutions, whose strength approaches that of tertiary amines such as triethylamine and trioctylamine.

The rules governing the formation of the basicity of the organoelemental oxo-bases R_nXO with X=S, Se, N, P, or As have been established in a series of studies[136-138]. Particular attention was devoted to the search for relations between the polar effects of the substituents and the basicity or the extracting capacity of the oxo-bases and also to the study of the distribution of the oxides between different phases as the H_2SO_4 concentration in the two-phase system is varied. The constants K_a were determined by Arnett's method. The results of the study showed that the extraction capacity of the oxo-bases is determined to a large extent by their basicity, which is influenced by the nature of the element X in the group XO and by the type of the substituent R. Among both aliphatic and aromatic derivatives, the strongest bases proved to be the oxides of arsenic, antimony, and selenium.

Potentiometric titration of the oxides of substituted aryldihydrophenarsazines in a mixture of acetic acid and acetic anhydride showed[139] that this medium does not have a differentiating effect on the basicities of the test compounds. More hopeful results are obtained when the basicities of the TAO of the type $XC_6H_4As(O)(C_2H_5)_2$ in acetic anhydride and nitromethane are compared[140]. The authors established that acetic anhydride exhibits a differentiating effect and that the pK_a of arsine oxides vary markedly as a function of the structure of the substituents X in the benzene ring. The mixture of nitromethane and acetic anhydride[141], which permits the titration of a wide variety of compounds of tetracoordinate arsenic, possesses such properties.

The determination of the basicity of weak bases in nitromethane by potentiometric titration with perchloric acid became possible after the improvements proposed in a number of investigations[142-144]. The study of the protonation of the oxides of organic derivatives of Group VB elements (nitrogen, phosphorus, and arsenic) by the above procedure made it possible for the first time to determine the pK_a in nitromethane for the derivatives investigated[145]:

$(C_8H_{17})_3PO$	9.72
$(C_8H_{17})_3NO$	16.85
$(C_8H_{17})_3AsO$	16.14

It was found that the protonation reaction proceeds in steps:

$$2R_3EO + H^+ \overset{K_{a_1}}{\rightleftarrows} R_3EO \ldots \overset{+}{H} \ldots OER_3;$$

$$R_3EO \ldots \overset{+}{H} \ldots OER_3 + H^+ \overset{K_{a_2}}{\rightleftarrows} 2R_3\overset{+}{E}OH.$$

On the titration curve, this is manifested by two distinct potential jumps corresponding to 50% ($E^{I}_{0-50\%}$) and 100% ($E^{II}_{50-100\%}$) neutralisation. The use of *N,N'*-diphenylguanidine as the reference standard ($pK_a = 17.2$) made it possible to adjust the observed half-neutralisation potentials $E^{I}_{1/2}$ and $E^{II}_{1/2}$ to the basicity constant scale of the test compounds in nitromethane, which permits in its turn the calculation of the overall basicity constants of the compounds and the equilibrium association constants of the bases in solution ($\lg K_{ass}$). Comparison of the pK_a obtained shows that trioctylphosphine oxide is a weaker base than the corresponding nitrogen and arsenic oxides whose basicities are similar.

Developing this concept further, Laskorin and coworkers determined the pK_a for a series of tertiary arsine oxides and sulphides in nitromethane[146,147]. It follows from the results that the basicity of arsine oxides in both water and nitromethane increases with increasing length of the hydrocarbon group R at the arsenic atom. The pK_a values in water and in nitromethane are linearly related which suggests that the mechanism of the protonation of arsine oxides in water and in non-aqueous neutral solvents is the same. It is noteworthy that the Ka of arsine oxides in nitromethane are higher than in aqueous solutions approximately by a factor of 10^{11} and that trialkylarsine oxides behave in this solvent as organic bases whose strength is not inferior to that of trialkylamines. The replacement of arsenyl oxygen by sulphur on passing from TAO to a trialkylarsine sulphides $R_3As(S)$ reduces the basicity of these compounds approximately by a factor of 10^9 compared with the corresponding arsine oxides. This confirms the adopted mechanism of the protonation of arsenyl compounds at the oxide oxygen, where the pK_a of arsine oxides constitute a relative measure of the electron density at the oxygen of the arsenyl group. The latter has been confirmed also by the linear relations between the pK_a and the σ constants of the substituents at the arsenic atom for a series of aliphatic-aromatic TAO (Table 1). The best correlations are achieved when the σ^{ph} and σ^* constants are used, the slopes of the resulting relations for the TAO being close to the slopes ρ for tertiary phosphine oxides[149]:

$$pK_a = 3.08 - 1.608\Sigma\sigma^{ph}; \quad r = 0.993, \quad n = 30$$
$$pK_a = 8.26 - 1.570\Sigma\sigma^*, \quad r = 0.980, \quad n = 30.$$

This demonstrates the similarity of the mechanisms of the transmission of the electronic influences via the phosphorus and arsenic atoms and eliminates the need for the introduction of specific arsenic substituent σ constants. A similar confirmation was obtained also in the study of the nucleophilicity of the TAO in the reactions with alkyl halides[150-172], where the rate of formation of the complexes is correlated with the constants σ^{ph}.

IV. ELECTRON-DONATING PROPERTIES OF TERTIARY ARSINE OXIDES

The electron-donating properties of the oxo-bases $RnEO$ (E = N, P, As, or Sb) are determined by the presence of the unshared (lone) electron pairs (LEP) of the oxide oxygen in the upper, energetically low-lying, non-bonding orbital. The first ionisation potentials I_D of these compounds, which determines their electron-donating capacities, refer to the removal of an electron from the molecular orbital (MO), the p_π orbitals of the oxygen atom making the dominant contribution.

Table 1. Parameters of the correlations between the acid dissociation constants of the conjugate acids of arsine oxides and the reaction of constants of substituents: $pK_a = pK_{a_0} - \rho\Sigma\sigma_i$.

σ_i	pK_{a_0}	ρ	r	s	n
σ *para.*	12.654	4.94	0.923	0.44	5
σ^{ph}*	9.619	1.742	0.964	0.33	10
$\sigma^{ph'}$*	8.932	1.835	0.982	0.23	7
σ^*	15.145	1.534	0.958	0.35	9
σ_I^{ph}*	12.996	0.807	0.941	0.42	10
$\sigma_I^{ph'}$*	16.629	0.718	0.989	0.17	8

* σ^{ph}, $\sigma^{ph'}$, σ_I^{ph}, and $\sigma_I^{ph'}$ were taken from Laskorin and coworkers[146,147].

The energies of formation $\Delta H°$ of the donor–acceptor bond (DA bond), the overlap integrals of the interacting atoms DA, and the ionisation potentials of the compounds I_D can serve as measures of the electron density at the donor atom whose LEP are involved in the formation of the donor–acceptor bond. Comparison of these data[173] with the pK_a values shows that none of the above parameters is correlated with the basicity of the compound. The absence of a linear relation between the basicity and the effective charge on the oxygen of the oxide group (δ_O) should be noted particularly, which conflicts with the widely held conviction that the two parameters are equivalent.

Consequently the electron-donating properties of the molecules cannot be characterised with the aid of the basicity of the compounds but require special consideration. Comparison of the enthalpies of formation of the DA complexes between the bases of the type of oxo-bases (B) and acceptors (A) leaves no doubt that there is no direct relation between the quantity δ_O and $\Delta H°_{AD}$. Many investigators believe that the enthalpy of formation of DA complexes is the most suitable parameter for the description of the electron-donating capacity of compounds in processes of the EDA type. Such processes may include the formation of intermolecular hydrogen bonds (IRHB). The most well-founded method of estimating the electron-donating capacity of molecules in the formation of IRHB involves the determination of the thermodynamic parameters of the formation of hydrogen-bonded complexes with a standard acid—phenol in solution in carbon tetrachloride. Bearing in mind that the entropy of this reaction is virtually constant, one may conclude that the change of Gibbs free energy in the series of compounds investigated is caused by the change in the energy of the DA bond formed. Thus the enthalpy $\Delta H°$ is a quantitative characteristic of the electron-donating properties of the TAO in processes of the donor–acceptor type (Table 2).

It has been established[176] that aliphatic arsenic oxides form solid 1:1 complexes with phenol, which have been isolated and recrystallised from appropriate solvents. After the interaction of TAO with catechol, complexes were isolated and their structure was investigated by X-ray diffraction; the strength of the hydrogen bond in these complexes is so great that they sublime without decomposition[177,178]. The products of the interaction of TPAO with aromatic amines and with acid amides are stable 1:1 adducts. Their structure has been established by infrared spectroscopy; they are molecular compounds with an $R_3AsO...H_2NR^1$ hydrogen bond[179]. Complexes with a similar composition are formed when TAO are mixed with toluene-*p*-sulphonamide : $R_3AsO...H_2NSO_2C_6H_4.CH_3$.[180] Much attention has been devoted to the study of complexes of TAO with hydrogen peroxide, which are formed when arsenic oxides are produced by the oxidation of tervalent arsenic derivatives. Infrared spectroscopic data established that the adducts of H_2O_2 with TPAO and triphenylphosphine oxide (TPPO) have similar structures and have a component ratio of 1:2; the components are linked via a hydrogen bond[181]. The presence of a strong TPAO...HO–OH hydrogen bond, much stronger than in the complex with phosphine oxide, has been demonstrated by a study of the infrared spectra of the solution of TPAO in methanol in the presence of an excess of H_2O_2.[51] The adducts of hydrogen peroxide with TAO are therefore formed quantitatively simply on mixing arsenic oxides in solution in toluene with 30% hydrogen peroxide[1].

Table 2. Thermodynamic parameters of the complex formation reactions between tertiary oxides and phenol in solution in carbon tetrachloride[174,175].

Compound	$-\Delta H^\circ$ (ΔA)	$-\Delta H_f^\circ$	K°_{298}	$-\Delta G^\circ_{298}$	$-\Delta S^\circ$
	kJ	kJ	litre mol^{-1}	kJ mol^{-1}	kJ K^{-1}
$(C_6H_5)_3AsO$	—	—	352	14.5	—
$(C_6H_5)_2As(O)C_8H_{17}$	33.4	29.7	3030	19.8	56.0
$C_6H_5As(O)(C_8H_{17})_2$	31.8	33.6	7960	22.2	47.0
$(C_8H_{17})_3AsO$	35.0	36.0	7840	22.7	47.6
$(C_2H_5)_3AsO$	35.7	—	2518	19.4	59.5
$(C_4H_9)_3AsO$	28.4	—	7142	21.8	44.7
$(C_{12}H_{25})_3AsO$	32.4	—	10000	22.7	44.6
$(C_{16}H_{33})_3AsO$	31.0	—	19596	24.4	37.9
$(cyclo\text{-}C_6H_{11})_3AsO$	35.5	38.3	20000	24.5	41.5
$(C_4H_9CH(C_2H_5)CH_2)_3AsO$	31.5	—	7062	21.9	46.7

Among the other molecular complexes of TAO, mention should be made of the adducts with sulphur trioxide formed in the absence of atmospheric moisture[182], the complexes with iodocyanogen, which exist in solution in two different forms[183], and molecular compounds with iodine[67,184,185]. The last compounds are the most important, since the energy of their formation and their physicochemical properties were studied in detail by Mulliken[186] in connection with the development of the theory of charge-transfer complexes. The energy of the DA bond in the complexes of TAO with molecular iodine depends on the structure of the group attached to the arsenic atom and varies within wide limits[67,184].

The examples examined show that the TAO are some of the strongest electron donors and form stable molecular complexes with molecules having a deficiency of electron density at one of the atoms or vacant orbitals. The wide variety of the possible products of such processes is still far from exhausted; presumably further development of this field will open up new prospects for the theoretical and practical employment of organoarsenic compounds.

V. COMPLEXES OF TERTIARY ARSINE OXIDES WITH METAL SALTS

The complex-forming properties of arsenic oxides in relation to metal ions have been known for a long time and tertiary arsine oxides are therefore widely used as ligands in coordination chemistry. The properties of TPAO, from which numerous complexes of different structure and stoichiometry have been obtained, have been investigated in greatest detail. The structure of the complexes of metal salts with triphenylarsine oxide has been studied in fair detail by Goodgame and Cotton[86]. On mixing alcoholic solutions of copper(II) salts with a solution of TPAO, the complexes $[Cu(TPAO)_2Cl_2]$ and $[Cu(TPAO)_2Br_2]$ were obtained. It has been suggested on the basis of the reflection and absorption spectra of these complexes in the visible and infrared regions, X-ray diffraction patterns of the powders, and a comparison of the results of the available data for complex nickel[187], cobalt[188,189], and manganese(II)[87] salts that the complexes synthesised have a tetrahedral configuration.

The enthalpies of solution of the complex $[Cu(MePh_2AsO)_4.ClO_4]ClO_4$ in 0.02M solution of ethylenediamine in dimethylformamide have been measured calorimetrically at 25 °C. Measurements have also been made of the enthalpies of solution of $MePh_2AsO$ and water in the above solvent. The enthalpies of formation of the solid complexes and the reactants in the condensed state have been calculated. Furthermore, calculations have been made of the dissociation energies of the gaseous complex ions and the stabilisation energies of the metal ions in the crystal field[190]. The possibility of synthesising complexes with transition metals by direct precipitation from acetone solution has been investigated[191]. The complexes $CuCl_2(TPAO)_2$ and $CoCl_2(TPAO)_2$ obtained have been identified by elemental analysis. The compounds have been compared with their analogues synthesised by the available literature methods. The synthetic procedures, compositions, and infrared spectra of the complexes of TPAO, trimethylarsine oxide (TMAO), and trioctylarsine oxide (TOAO) with copper have been described[88,192,193].

The complexes of cobalt(II) salts with TPAO and the bidentate compound $Ph_2As(O)(CH_2)_n(O)AsPh_2$ (henceforth designated by L) have been isolated. It has been established that the TPAO forms complexes with a tetrahedral structure in perchlorate solutions and with a distorted octahedral structure in nitrate solutions. The reaction of the dioxide with cobalt(II) gives rise to complexes of the type $LCo(NO_3)_2$ (I), $[L_2(H_2O)_2Co](ClO_4)_2$ (II), and $[L_2Co](ClO_4)_2.2H_2O$ (III). The crystal structures of the complexes have been determined by magnetic and spectrophotometric analysis. It has been suggested[194] that complexes (I) and (II) have the octahedral structure and complex (III) the tetrahedral structure[194]. Somewhat earlier the cobalt complexes were obtained also by other workers[195]. The ligands employed were trimethyl- and tribenzyl-arsine oxides. The cobalt complexes with various TAO have also been examined in a number of other studies[88,192,193,196–198].

Studies of the infrared spectra of the complexes of TPAO with bivalent metal salts of the type ML_2X_2 (where X = Cl, or Br; M = Mn, Fe, Co, Ni, Cu, or Zn), showed that the stretching vibration frequencies of the AsO bonds occur in the range 840–910 cm^{-1}.[88] The authors believe that the coordination of the oxide to the metal salts increases the $\nu(As=O)$ frequency as a result of the superposition of the arsenic–oxygen

and metal–oxygen bond vibrations, which alter only slightly the position of ν(As=O) in the spectrum. In the spectra of similar complexes with methyldiphenylarsine oxide ν(As=O) is at 875 cm^{-1} and there is a shoulder at 866 cm^{-1} as a result of the superposition of the vibrations of the methyl group and the stretching vibrations of the AsO bond.

Phillips and Tyree[193] obtained a whole series of coordination compounds of TPAO with chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), zinc(II), mercury(II), tin(IV), antimony(III), and antimony(V) salts. In their studies on the infrared spectra of these compounds, the authors concluded that the arsenic–oxygen bond has some double bond character as a result of the p_π–d_π overlap of the occupied *d* orbitals of oxygen with the vacant *d* orbitals of arsenic. The coordination of the oxide to electron acceptors reduces the electron density of the π orbital and diminishes at the same time the bond multiplicity and the ν(As=O) frequency.

Generally speaking the ν(As=O) frequency tends to decrease on complex formation, which indicates a decrease of the bond order; the spectra shift on complex formation can be fairly significant. Thus the shift in the spectrum of the complex $HgCl_2$.TPAO reaches 70 cm^{-1}.[92] The change in the ν(As=O) vibrational frequency on complex formation with manganese salts, where the shifts can be both bathochromic[88] and hypsochromic[87,88], is an exception.

The complexes of zinc salts with TPAO and TMAO have been investigated[87,88,189,192,193,196]. The complex $Ni(TPAO)_4.(ClO_4)_2$ was first synthesised in 1971 [199] and was found to have three different isomers. The magnetic moments of all the isomers were determined, chemical analysis was carried out, and the melting points, electronic absorption spectra, and reflection spectra were measured. The results of the study of the nickel complexes with different TAO have been published[17,87,88,189,192,193]. The complexes of molybdenum(V) with TAO,[200] obtained by methods proposed previously[22,201], have been investigated by EPR. Compounds analogous to those already described[22,201] are formed in solution. Analysis of the EPR spectra led the authors to propose two possible structures of the molybdenum complex with a *cis*- and *trans*-disposition of the arsenic-containing ligands in the coordination sphere. The molybdenum(V) complexes of triphenylarsine oxide were also examined in another study[202].

The interaction of $UO_2(CH_3COO)_2.2H_2O$ with TPAO on refluxing in ethanol led to the isolation of the complexes $UO_2TPAO.nC_2H_5OH$.[203] The presence of the 860 cm^{-1} band in the infrared spectra of the complexes confirmed that the formation of complexes with UO_2^+ involves the oxygen of the AsO group. Bearing in mind the high melting point and low solubility of the complex in organic solvents, a polymeric structure was proposed for it with bridging oxygen atoms. The synthesis of the monomeric complexes $UO_2(CH_3.COO)_2.L_2$ and $UO_2[(C_2H_5)_2NCS]_2.L$ and the dimeric complex $[UO_2(CH_3COO)_2.L_2]_2$, where L=TPAO, has been described in a series of communications[204–208]. X-Ray diffraction studies have been made on the compounds obtained, their lattice parameters have been calculated, their molecular weights and molar conductances have been determined, and their infrared spectra have been measured. It has been established that the uranium atoms in the monodentate complex occupy positions at the centres of symmetry of the crystal lattice. The structural parameters of the dimeric complex have been determined by X-ray diffraction and it has been established that uranium(VI) has a coordination number of 7 and that dimerisation takes place via bridging acetate groups.

The complexes of $[UO_2(C_4H_2S_2N)_2]^{2-}$ with TPPO and TPAO have been synthesised and identified by elemental analysis and on the basis of their physicochemical characteristics (colour, melting points, electrical conductivities, and infrared spectra)[209]. It was established that TPAO is a more powerful donor and that the U–O bond in its complex is therefore weakened to the maximum extent. The infrared spectra (in the range 200–500 cm^{-1}) of the complexes $UO_2X_2L_2$ (L=TPAO or TPPO; X=Cl, Br, NO_3, or NCS) have been studied in detail[210]. Comparison with the spectra of the caesium and rubidium complexes[210] enabled the author to carry out new or corrected assignments of the absorption bands. Thus the intense band in the range 247–265 cm^{-1} was assigned to the O–U–O deformation vibrations instead of the metal–nitrate stretching vibration proposed previously. The U–O stretching vibration frequencies in the complexes were found to lie in the range 435–440 cm^{-1}, which indicates unambiguously a stronger bond in the complex with TPAO compared with TPPO. The infrared spectra of TPAO with uranyl nitrate and uranyl chloride have been investigated. In all the cases studied the asymmetric stretching vibration frequency of the AsO group decreases. The values of ν(As=O) have been published for the complex $UO_2(NO_3)_2.2TPAO$, namely 868 cm^{-1} [211] and 862–870,[212,213] while the frequency found for the complex $UO_2Cl_2.2TPAO$ was found to be 848 cm^{-1}.[212] The symmetrical stretching vibration frequency of the U–O group is observed in all cases in the range 910–925 cm^{-1}.

Recent conductimetric and potentiometric studies in anhydrous media demonstrated yet again[214,215] that the ligands containing AsO exhibit a greater capacity for the substitution of chloride ions in the coordination sphere of the uranium atom in UCl_4 than their analogues with the PO linkage. It has been shown by X-ray crystallography that the crystal structure of the complex $UCl_4.2TPPO$ varies as a function of the type of the phosphine oxide substituent[215]. By analogy, the authors decided to investigate the structure of the complex of an arsine oxide with UCl_4. They decided to determine whether or not the strong interaction of the oxygen with uranium leads to a decrease of the U–O bond length. The first compound in the test series was the complex of UCl_4 with triethylarsine oxide. The resulting molecule proved to be centrally symmetrical with four chlorine atoms located in the same plane as uranium and two oxide ligands coordinated to the uranium atom in the *trans*-positions, which leads to the distortion of the tetragonally octahedral arrangement. The bond lengths and the angles are similar to those found previously, but it was discovered that the increase in the length of the UCl bond in the complex with arsine oxide is accompanied by actual shortening of the U–O bond. All the measurements demonstrated convincingly that the interaction with U–O in the example investigated is much stronger than those observed in a wide variety of complexes of phosphine oxides with UCl_4.

The complex of triphenylarsine oxide with $Pu(NO_3)_4$, having the composition $Pu(NO_3)_4.2TPAO$, has been studied in detail[216]. The above communication gives the method of synthesis and infrared spectroscopic data in the range from 200 to 4000 cm^{-1}. It has been established that on complex formation the asymetric stretching vibration frequency of the AsO bond decreases, which is consistent with data obtained previously in the study of the formation of complexes of uranyl nitrate with TPA.[211–213]. As a rule the ν(As=O) frequency is not split on complex formation and in the spectrum of a plutonium complex of TAO there is an intense single band at 850 cm^{-1}. The spectrum of the complex in the visible region indicates the presence of only tetravalent plutonium, although its coordination number is 10. High coordination numbers of the thorium(IV) and thorium(III) complexes had been found previously by X-ray diffraction, amounting to 11 and 12 respectively[217].

Comparison of the frequencies of the nitrato-groups in the plutonium complex with those found earlier for $UO_2(NO_3)_2$. .2TPPO [218] showed that the agreement between them is satisfactory. Bullick[211] assigned the bands at 1515, 1282, 1028, 1032, and 809 cm^{-1} to nitrato-groups, which is fully consistent with data obtained for the plutonium(IV) complex of triphenylarsine oxide[216], where the nitrato-group exhibits bidentate coordination. The 420 cm^{-1} band, observed in the plutonium complex of TPPO, is absent from the spectrum of the TPAO complex. However, a band at 377 cm^{-1} appears in the spectrum of the latter complex, which the authors[216] assigned to the asymetric stretching vibration of the Pu–O bond in the plutonium–oxygen–arsenic group. This assignment is in good agreement with the results of an earlier study of the complexes $MCl_2(TPAO)_2$, where M = Mn, Fe, or Co.[88]

By mixing boiling alcoholic solutions of TPAO and salts of the type $M(NO_3)_3$ (in different molar proportions), where M(III) represents lanthanide elements and yttrium, crystalline complexes of different compositions were obtained[219]. The authors suggested that the alcohol molecule in the complex is coordinated to the M atom and that the complex is a polymer containing NO_3 bridging groups. Infrared spectroscopic data led to the conclusion that the TPAO–M bond is much more stable than the analogous bond in the complexes with triphenylphosphine oxide. A considerable thermal stability of the complexes with the organoarsenic compound compared to the analogous complex with TPPO was noted.

Complexes of lanthanum(III), neodymium(III), and samarium(III) oxides with ethyldiphenylarsine oxide (L) have been synthesised[220]. The complexes isolated were investigated by elemental, magnetic and spectrophotometric analyses. It was established that they are consistent with the fundamental formula $Ln_2Cl_6L_3.xH_2O$ ($x = 0–2$). The high melting points and limited solubilities of the majority of the organic diluents indicate the polymeric nature of the complexes.

More than 25 complexes of the type SnX_4L_2 (where X = Cl, Br, or I; L = TPPO or TPAO) have now been obtained[221]. All the complexes synthesised have been characterised by their infrared spectra and it has been established that in the above series only the *trans*-isomers are produced, with the exception of bidentate structures. A strengthening of the Sn–O bond has been noted and the authors[221] believe that this is caused by the smaller electronegativity of arsenic, the higher polarisability of TPAO, and the smaller contribution of π-bonding in AsO. The tin complexes of triphenylarsine oxide have also been investigated in other studies[193,222–224]. Apart from tin halides, the TAO also react with organotin compounds to form singly- and doubly-charged cationic complexes[225,226], whose structure has been investigated by infrared and ^1H NMR spectroscopy.

It is noteworthy that there is no literature data for the complexes of TAO with alkali metal cations. The complexes $SbCl_3$.2TPAO, $SbCl_3$.2TPPO, $BiCl_3$.2TPAO, and $BiCl_3$.2TPPO have been synthesised and their vibrational spectra investigated in the range 30–1700 cm^{-1}. The structural effects have been examined in terms of the principle of the correspondence between the ν(P=O) and ν(As=O) frequency shifts and the Lewis acidity and basicity of the ligands and the coordination numbers have been calculated. It was established that the difference between AsO and PO is as expected, i.e. TPAO is a stronger base, which is confirmed also by the difference between the metal–oxygen stretching vibration frequencies. A polymeric structure, characteristic also of complexes of heavier elements[227,228], has been proposed for the above complexes. The study of the complex $HAuCl_4$.2TPPO established that the phosphine oxide molecules are not coordinated directly to the metal atom but form a bond with a proton of the chloroauric acid. The complex $[H(TPAO)_2]$. .$AuCl_4$, whose structure is close to that of the complex examined above, was synthesised by an analogous procedure and investigated[229].

The determination of the heats of complex formation made it possible to set up a series based on the electron-donating capacities of different ligands in relation to antimony pentachloride ($Ph_2SeO \cong Ph_3AsO > Me_3PO > Me_2SO$) and tin tetrachloride ($Ph_2SeO \cong Ph_3AsO > Me_3^1PO > Ph_3PO$).[230] The most probable cause of the change in the electron-donating activity is the decrease in the above series of the negative charge on the oxygen atom of the ligand molecule and hence an increase of the multiplicity of the EO bond. The example quoted shows that TPAO is in both cases a fairly powerful ligand, i.e. a compound with a considerable charge at the oxygen atom and a relatively small multiplicity of the bond between the arsenic and oxygen atoms.

Complexes of the type $M(O–O)F_3(TPAO)_2$, where M = Nb or Ta, have been synthesised by a standard method[231]. They are sparingly soluble in organic solvents. The molar conductances indicate a molecular structure of the complexes, which were characterised by the results of elemental, X-ray diffraction, and spectroscopic analyses[231]. The interaction of niobium and tantalum pentachlorides with TPAO led to the formation of complexes with a polymeric structure[232].

Several complexes of manganese(II) salts with TPAO and TPPO are now known, but their stability in air and at room temperature is limited, which significantly hinders their investigation[233]. Our knowledge about their stoichiometry and magnetic and spectroscopic properties is therefore extremely incomplete. The ligands mentioned above have high dipole moments, which in some cases favours the stabilisation of the transition metal complexes, as, for example, in the case of manganese(III) salts. In this connection, synthetic procedures, the results of elemental analyses, and the spectroscopic and magnetic properties of the complexes $Mn(TPPO)_3Cl_3$ and $Mn(TPAO)Cl_3$ have been described. The complexes synthesised are stable in most solvents. Data have been published[233] on their molar conductances in acetone and nitromethane and on their infrared spectra in the range 250–4000 cm^{-1}. The manganese compounds have also been investigated in other studies[87,88,189,192,193].

The reversible and irreversible reactions of iron(III) with the organic bases TPPO and TPAO have been investigated[234] and the equilibrium constants for the formation of 1:1 complexes of TPAO have been determined. It was established that the formation reaction of the complex is a first-order process. The spectra of the adducts have an absorption maximum in the region of 510 nm (TPAO) and 480 nm (TPPO). Complexes of TPAO with iron(II) [235] and mercury(II) [236] salts have been obtained. It has been established that the compounds synthesised have a tetrahedral structure. The iron(II) and iron(III) complexes with trimethyl- and triphenylarsine oxides have been investigated[88,192,193,236].

Rhenium complexes have been described[237,238]. Studies have been made of the complexes of BF_3 with sulphoxides and amine, phosphine, and arsine oxides of the type $R_nXO.BF_3$ (R = Me or Et).[239] The ^1H, ^{11}B, and ^{19}F NMR spectra (at different temperatures) and the ^{31}P NMR spectra have been measured[239]. Data have been published on the complex-forming properties of tribenzylarsine oxide[240].

In conclusion of the discussion of the numerous studies on the complexes of TAO with different metals, one should note that the bond in the complexes investigated is in all cases stronger than in the analogous complexes with organophosphorus compounds. This property of TAO has been used widely in coordination chemistry for the synthesis of new

complexes, which extends our ideas concerning complex formation in aqueous and non-aqueous solutions.

VI. EXTRACTION OF PROTIC ACIDS AND WATER

The greatest number of studies in this field are associated with the extraction of nitric acid. The ability of trialkylarsine oxides or their hydrates to interact with dilute nitric acid in an alcoholic medium has been pointed out in a number of studies[30,241,242]. As a result of such interaction, it has been possible to obtain crystalline salt-like adducts [Alk_3.AsOH]NO_3. The adducts of nitric acid with alkylarylarsine oxides[14,29,30,121] and trialkylarsine oxides[30,57,89,243] are also known.

Numerous X-ray diffraction, infrared spectroscopic, and spectrometric data for the adducts of acids with TAO established two possible structures of the latter in the solid state:

(a) $R_3AsO...HX$—structure presupposing the presence of a hydrogen bond;

(b) $[R_3AsOH]^+X^-$—ionic structure.

The structure of the 1:1 adducts of TAO with acids depends in each specific case on numerous factors, the principal of which are the nature of the acid anion and the strength of the base.

In a study of the electrical conductivity of the adducts of triphenylarsine oxide with nitric acid in acetonitrile it was established[243] that the adduct partly ionises under the influence of the solvent. In addition, the interaction of Rh_3AsO or its hydrate with concentrated HNO_3 yielded triphenylarsine dinitrate $Ph_3As(NO_3)_2$. The compound is extremely hygroscopic and readily hydrolyses in the presence of traces of moisture. A crystalline complex of triphenylarsine oxide with nitric acid precipitates from a solution of triphenylarsine dinitrate in acetone treated with petroleum ether. A detailed study of the extraction of nitric acid has been carried out[244] and the authors showed that the interaction of the acid and the organic base takes place in steps and reduces to a gradual substitution of the water molecules in the structure of the hydrated extractant. Thus at a HNO_3 concentration of 0.1–1.0M the product is a 1:1 adduct with coextraction of water. With increase of the acid concentration, the acid : reagent ratio increases with a corresponding decrease of the water : acid ratio.

It has been suggested[244] that the complex has the composition $R_3AsO.XHNO_3.YH_2O$ with variable values of X and Y depending on the concentration of nitric acid in the aqueous phase and of the extractant in the organic phase. The nature of the associated species formed by water and nitric acid with the organic base has been studied in detail[245,246]. The extraction of HNO_3 into solutions of triphenylarsine oxide in dichloroethane has been studied by both partition and infrared spectroscopic methods. The fractions of free, hydrated, and protonated oxide were determined as logarithmic functions of the ionic activity of nitric acid in the aqueous phase, which was calculated from the corresponding (adjusted to the equilibrium activity of water in the aqueous phase) hydration constants, the protonation constant, and the ionic activity of nitric acid. It was noted that in the case of trioctylphosphine and triphenylarsine oxides the concentration of free oxide (relative to triphenylphosphine and tribenzylphosphine oxides) is too low to be taken into account.

The determination of the energetic characteristics of the hydration of neutral arsenyl compounds is necessary both from the point of view of understanding and a quantitative description of the extraction processes and for the establishment of the electron-donating capacities of these derivatives using water as the reference electron acceptor[247]. For this purpose, the standard enthalpies ΔH°, entropies ΔS°, free energies ΔG°_{298}, and equilibrium constants K^θ of the process[248]:

$$R_3As(X) + H{-}O{-}H \rightleftarrows R_3As(X)\ldots HOH \quad (X=O,\ S)$$

were determined in CCl_4 solution by infrared spectroscopy.

When water is added to solutions of TAO in CCl_4, a narrow intense band at 3700 cm^{-1} (ν_S) and a broad diffuse band at 3280–3300 cm^{-1} (ν_{as}) appear in the infrared spectra, their intensity increasing with increasing concentration of water in the solution. At the same time the stretching vibration frequency of the arsenyl group $\nu(As=O)$ shifts from 890 cm^{-1} to 875 cm^{-1}, which implies that the complex $R_3AsO...H_2O$ is formed under the experimental conditions via an intermolecular hydrogen bond between the water protons and the unshared pairs of the oxygen atom of the arsenyl group.

The calculated hydration constants of arsine oxides are significantly higher than those obtained for phosphine oxides[247]. Contrary to expectation, the replacement of alkyl groups at the arsenic atom by aryl group has little effect on the hydration constants, which decrease only slightly in the sequence trioctylarsine oxide > dioctylphenylarsine oxide > octyldiphenylarsine oxide. The sequence of hydration constants for arsine oxides is fully consistent with the reactivity series calculated on the basis of the complex formation reaction with phenol. The hydration of arsine oxides in solution in CCl_4 is an isoenthalpic reaction, like their complex formation reaction with phenol[174].

In contrast to arsine oxides, arsine sulphides $R_3As=S$ are weaker bases and the constants for the formation of their complexes with water are lower. In solution in CCl_4 it is impossible to determine the hydration constants of these compounds owing to the low concentration of the hydrated form even under the conditions of the complete saturation of the organic solution with water. The equilibrium constant for the process changes little with the length and structure of the groups at the arsenic atom and these changes are wholly determined by entropic factors. In contrast to this, the thermodynamic characteristics of the hydration reaction of phosphoryl compounds depends significantly on the nature of the substituents at the phosphorus atom[249]. Thus the changes in the reactivity of the organophosphorus and organoarsenic extractants in the hydration reaction are due to different causes, which must be taken into account in determining the relation between the electronic structure of these compounds and their reactivity.

The infrared spectra of organic solutions of TPPO and TPAO saturated with nitric acid (equilibrated with an aqueous HNO_3 solution) have two fundamental features[245,246]: (a) with increase of the activity of nitric acid, the intensity of the characteristic absorption bands of the monohydrate falls; (b) the PO and AsO stretching vibrations are displaced towards lower frequencies. The latter data yield reliable information about the nature of the bond between nitric acid and the phosphoryl or arsenyl oxygen in the protonated form. More detailed information about the nature of the bond in the complex $TPAO.HNO_3$ was obtained with the aid of the infrared spectra of the organic phase equilibrated with 2M acid and also the infrared spectra of the solid deposit $TPAO.HNO_3$ in an emulsion with hexachlorobutadiene[246]. The considerable (~100 cm^{-1}) splitting of the ν_3 band due to the antisymmetric vibration of the nitrate ion at 1380 cm^{-1} indicates the interaction of the nitrate ion with the cation. The authors attribute it to a protonated structure of the type $TPAO...H^{\delta+}-NO_3^{\delta-}$ with incomplete transfer of the proton. The possible structure of the mixed associated species can be represented

in the following form on the basis of the analysis of the infrared spectra:

$$\begin{matrix} \text{TPAO}\ldots\text{H} \\ \text{TPAO}\ldots\text{H} \end{matrix}\!\!>\!\text{O}\ldots\text{H}^{\delta+}\!-\!\text{NO}_3^{\delta-}\ .$$

The hypothesis of the partial proton transfer from the acid to the oxygen atom of water was subsequently confirmed by the absence of bands due to the H_3O^+ ion in the spectrum of the mixed associated species. Analogous results had been obtained earlier[244]. According to Rozen and Nikolotova's data[250], the complex TPAO.HNO_3, where nitric acid fully displaces water from the organic phase, is extracted into the latter. Similar conclusions were reached in the study of the infrared spectra of solutions of trioxylarsine oxide in CCl_4 after contact with water and nitric acid[251]. The decrease of the intensity of the absorption bands due to the stretching vibrations of free and bound water at 3695 and 3350 cm^{-1} and the $\nu(As=O)$ band at 890 cm^{-1} indicates the displacement of nitric acid by water from the organic phase and the formation of the monosolvate $R_3AsO.HNO_3$.

When the benzene ring is replaced by the octyl group under comparable conditions, the HNO_3 extraction constant increases by a factor of almost 7 in the sequence of $Ph_3AsO < Ph_2As(O)Oct_2 < PhAs(O)Oct_2 < Oct_3AsO$.[251] The extraction constant also increases with increasing length of the group R on passing from aliphatic to alicyclic substituents (Table 3). The extraction capacity of arsine oxides is linearly related to their reactivity in processes of the donor–acceptor type, which confirms in its turn the qualitative conclusions concerning the decisive role of the basicity of arsine oxides in the liquid extraction of inorganic acids and salts. At the same time there are no grounds for isolating trialkylarsine oxides in a separate group of extractants, extracting nitric acid via special mechanisms different from that of extraction by TPAO. It is most probable that one is dealing with a purely quantitative increase of the extraction constant as a result of the replacement of aryl groups by alkyl groups. In this case arsine oxides are full analogues of phosphine oxides for which such properties are well known.

Table 3. Effective constants for the extraction of nitric acid from aqueous solutions by solutions of arsine oxides in carbon tetrachloride[251].

Extractant	$\bar{K}_{HNO_3}$	Extractant	$\bar{K}_{HNO_3}$
$(C_6H_5)_3AsO$	2 220*	$(C_8H_{17})_3AsO$	16 020
$(C_6H_5)_2As(O)C_8H_{17}$	7 630	$(C_9H_{19})_3AsO$	21 390
$C_6H_5As(O)(C_8H_{17})_2$	10 910	(cyclo-$C_6H_{11})_3AsO$	37 250

* In dichloroethane.

The results obtained demonstrate a sharp (by a factor of 10^3) increase of the extraction capacity of arsine oxides compared with their organophosphorus analogues. This phenomenon is difficult to account for, particularly since some workers have adopted the concept of the p_π–d_π conjugation of the unshared electron pairs of the arsenyl oxygen with the vacant 4d orbitals of the arsenic atom. In this case the entire difference between the organophosphorus and organoarsenic compounds reduces to a slight difference between the electronegativities of the phosphorus and arsenic atoms (2.19 and 2.18) and the longer bond lengths for arsenic owing to the greater radius of the latter ($r_P = 1.10$ Å, $r_{As} = 1.21$ Å), while the hybridisation is virtually the same.

These differences do not explain the considerably greater basicity and reactivity of the arsenyl compounds and also the different energy and force constant of the $\geqslant$As–O bond. The model of the arsenyl group with the coordinate bond $\geqslant As^+-O^-$ and only slight conjugation of the arsenyl oxygen with arsenic is more justified. In this case TAO are more likely to be analogues of *N*-oxides than phosphine oxides, which is manifested when the reactivities of these classes of compounds are compared.

Bearing in mind that one of the causes of the increase of the reactivity of the compound R_3EO is the size of the atom E, a number of workers[252–256] attempted to classify the changes in extraction capacity in the series R_3NO–R_3PO–R_3AsO–R_3SbO ($r_N = 0.75$ Å, $r_P = 1.11$ Å, $r_{As} = 1.24$ Å, $r_{Sb} = 1.41$ Å). The increasing basicity of oxygen when phosphorus is replaced by arsenic is caused, in their view, by the decrease of the energy of the element–oxygen bond, as shown by the infrared spectroscopic data for the oxides of the trialkyl derivatives of Group VB elements: $\nu(P=O) = 1170$ cm^{-1} and $\nu(As=O) = 884$ cm^{-1}. The force constant for AsO is smaller by a factor of 1.47 than for PO. The bond energy is reduced as a consequence of the increase of the interatomic distance and also apparently owing to the difficulty of the interaction of the 2p electrons of oxygen with a vacant 4d orbitals of arsenic. Furthermore, the changes in extraction capacity in the series $R_2CO < R_2SO < R_3PO < R_3AsO < R_3SbO$ is explained also by the different electronegativities of the elements, which decreases in the above series of extractants as a consequence of the variation of the amount of ionic character of the element–oxygen bond, the degree of covalence, and bond strength.

The structure of the groups R at the arsenic atom has a significant influence on the partition of nitric acid between water and organic phases. The claim[252] that the mechanism of the extraction of nitric acid changes abruptly on passing from aryl to alkyl organic derivatives of tetracoordinate arsenic is problematical. The authors put forward the variant[252] in which the increase of the basicity of the compound leads to the replacement of the hydrogen bond by proton transfer. Incidentally, in the last study by the same investigators[257], devoted to the formation of complexes by nitric acid with phosphine, arsine, and amine oxides, a linear relation was established between the degree of extraction of nitric acid and the number of phenyl substituents in the molecules of TAO, which disproves an abrupt alteration of the properties in the given reaction series.

Noting the appreciable progress in the study of the extraction of nitric acid by TAO achieved by Rozen et al.[257], we may remark that their conclusions[257] and those of the present authors[251] are quite identical although the two groups of investigators base them on different extraction mechanisms (solvate and ionic respectively). It is extremely probable that the properties of nitric acid extracts in the systems investigated depend significantly on the experimental conditions such as temperature, the type of diluent employed, and the concentrations of the extractant and acid. One can claim with much justification that the extraction of nitric acid by dilute solutions (<0.01M) of TAO in CCl_4 at 25 °C and an HNO_3 concentration <0.01M proceeds via the solvate mechanism. This is supported by the internally consistent linear relations between the free energy of the extraction of HNO_3 and the analogous quantities for donor–acceptor processes[258].

The parallel variation of the free energies of all the reactions considered with the structure of the groups attached to the arsenic atom for a constant reaction centre (arsenyl oxygen) shows that there is no doubt that the donor–acceptor

processes involving TAO obey linear free energy relations (Table 4). For the reactions of arsenyl compounds with acids in organic solvents, the best results have been obtained using the constants σ^*, which ensure high correlation coefficients r for low values of s. The use of the resonance constant σ_R and the overall constants σ, describing the joint inductive and resonance influence of the substituents on the reaction centre, proved successful only for Kabachnik's overall constants σ^{ph} introduced for substituents attached directly to the phosphorus atom.

Table 4. Relation between the free energies (kJ mol^{-1}) of donor–acceptor processes and the reaction constants of substituents: $-\Delta G_i = \Delta G_0 + \rho\Sigma\sigma_i$.

ΔG_i	σ_i	ΔG_0	ρ	r	s	n
$-\Delta G^0_{HNO_3}$	σ^*	23.65	−0.5494	0.94	0.1824	5
$-\Delta G^0_{HNO_3}$	σ^Φ	13.73	−0.7779	0.96	0.1499	5
$-\Delta G^0_{H+(CH_3NO_2)}$	σ^*	6.72	−0.0643	0.97	0.0124	9
$-\Delta G^0_{H+(CH_3NO_2)}$	σ^Φ	5.76	−0.0751	0.96	0.0145	10
$-\Delta G^0_{H+(H_2O)}$	σ^*	3.06	−0.1546	0.99	0.0182	6
$-\Delta G^0_{H+(H_2O)}$	σ^Φ	0.78	−0.1861	0.95	0.3122	6

Thus, within the limits of the series of compounds investigated, the description of the reactivity of arsenyl compounds in processes of the EDA type does not require the introduction of new constants for substituents attached directly to the arsenic atom and one can employ the tabulated σ^* and σ^{ph} constants. The above correlation analysis also permits the conclusion that the mechanism of the transmission of electronic influences in the molecules of organoarsenic compounds is predominantly inductive. At any rate, the resonance interaction between the benzene ring and the arsenic atom observed by physicochemical methods in aromatic arsine oxides does not have an appreciable influence on the reactivity of the organoarsenic compounds. The correlation of the electron-donating capacity of arsine oxides with the overall constants σ^{ph} does not conflict with the inductive model of the transmission of the electronic influences in the molecules of organoarsenic compounds[259], since according to some investigators[258] the inductive component predominates in σ^{ph}.

It is noteworthy that no less attention has been devoted to the study of the products of the interaction of TAO with hydrogen halides than to the extraction with nitric acid. However, the proposed extraction system with HCl has still been relatively little investigated. The model of the extraction with HCl is analogous to that proposed previously for nitric acid, i.e. with increase of the concentration of the acid its molecules displace water molecules combined with the organic base[244]. The infrared spectra of the solid adduct of hydrochloric acid with TPAO have been investigated and the authors observed a complex high-intensity absorption in the range 2000–2750 cm^{-1}, which is a feature of the hydroxy-group involved in a strong hydrogen bond [57]. The behaviour of the adduct in acetonitrile made it possible to classify it as a weak electrolyte.

The oxides of 10-alkyl(aryl)-5,10-dihydrophenarsazines react with HCl in an aqueous alcoholic medium or boiling benzene and give rise to a 1:1 adduct[260]. According to the authors, the structure of the adduct presupposing the presence of a hydrogen bond without proton transfer is the most probable. A detailed study of the HBr and HI systems showed that the extraction behaviour of the two acids is similar[244]. Thus, at an initial concentration of the aqueous acid of 0.1–2.0 M they give rise to 1:1 adducts. The coextraction of one mole of water for each mole of the acid is observed also below the concentration indicated. The tertiary arsine oxide–HBr and HI systems have also been studied in other investigations[57,89,260]. Special experiments[261] demonstrated the possibility of isolating tertiary arsine dihalides as a result of the interaction investigated. It was found that, in the presence of a sufficient excess of the acid, the dihalides become the main reaction products, which is only possible when their resistance to hydrolysis is fairly high.

Among all the acids investigated, perchloric acid exhibited the most distinctive extraction characteristics[244]. Saturation is attained at an acid concentration of 0.1 M and the resulting adduct has the composition $R_3AsO : HClO_4 = 1:1$. It has also been established that each mole of water is coextracted with a mole of perchloric acid entering the organic phase. The interaction of perchloric acid with TPAO has been studied in detail[57]. The compound obtained contained the triphenyloxyarsonium cation, since the high measured conductivity in acetonitrile (λ, cm^2 equiv.$^{-1}$ Ω^{-1} > 100) showed that the compound has an ionic structure. It is known that chloroacetic acids can be arranged in the sequence monochloroacetic acid < dichloroacetic acid < trichloroacetic acid in terms of their strength. Spectroscopic study of the products of the interaction of TAO and the acids in proportions of 1:1 showed that the infrared spectra of the solid adducts can be divided into three types[89,134,262].

1. The infrared spectrum of the adduct of the base with the weak monochloroacetic acid contains three main bands in the range 1800–3000 cm^{-1}. The intensity of these bands changes in accordance with the strength of the acid or the base. A weak hydrogen bond is characteristic of such adducts.

2. The bases investigated form adducts with the strong trichloroacetic acid, whose spectrum does not contain bands characterising the hydroxy-group but there is a broad and intense band in the region of low frequencies. The $\nu(As=O)$ band shifts towards lower frequencies. The spectrum is analogous to those of substances with symmetrical hydrogen bonds without proton transfer to the oxygen of the base. According to the above investigators, the strongest hydrogen bond is characteristic of such adducts. It has also been established that a change in the state of the substance does not entail considerable changes in the spectrum. Analogous results were also obtained by Abalonin et al.[260].

3. The spectrum of the adducts of dichloroacetic acid with TPA changes with the state of the substance[262]. The authors regard this as an intermediate spectrum between the two spectra discussed above. The study of the infrared spectrum of the adducts of dichloroacetic acid with trimethylarsine oxide demonstrated a strong hydrogen bond with proton transfer[262]. A triplet at 1720, 1655, and 1580 cm^{-1} in the region of the band of the antisymmetric vibrations of the CO_2 group was isolated in the spectrum. The addition proton bands at 1720 and 1580 cm^{-1} disappear on deuteration.

The ability of tertiary arsine oxides to interact with picric acid with formation of a crystalline salt is frequently used to isolate them[29,263–265]. It has been established that methylenebis(diphenylarsine) oxide reacts with picric, styphnic, and picrolonic acids, forming the corresponding hydroxypicrates, hydroxystyphnates, and hydroxypicrolonates[16].

The data considered in this Section show that the interaction of TPAO with protic acids (Brønsted acids) is a complicated process whose mechanism is determined by the type of

acid considered. Changes in the structures of the groups attached to the arsenic atom have little influence on the extraction capacity of the compounds, causing purely quantitative alterations within the limits of a single extraction mechanism. On the other hand, a change in the type of acid extracted frequently alters the nature of the interaction of the acid with the extractant from complexes with a weak hydrogen bond to the formation of purely ionic structures. This property of organoarsenic extractants must be carefully taken into account in the study of the extraction of metal salts from acid aqueous solutions.

VII. EXTRACTION OF METAL SALTS

The study of the complex-forming capacity of different classes of organoarsenic compounds led to the discovery of certain effective extractants among them. Thus in a series of studies Rozen and coworkers[250,252-256] investigated the influence of the structure of the reaction centre on the extraction and compared the extraction capacities of trioctylphosphine, triphenylarsine, and trioctylarsine oxides. They established that the reaction capacities of the organophosphorus and organoarsenic oxides are approximately described by a common equation, the maximum extraction capacity being virtually obtained for arsine oxides. It was noted that, in contrast to the extraction with R_3PO, inorganic acids cannot displace metals from the organic phase containing aromatic arsine oxides[250,252-256].

The extraction of metal anions of the type ReO_4^- and TeO_4^- from a 1M solution of hydrochloric acid has been studied. The extraction constants obtained differentiate appreciably the organoarsenic compounds from their phosphorus-containing analogues. The authors[252-256] see the cause of this finding in the different capacities of the oxides for protonation due to the nature of the PO and AsO bonds[137].

The possibility of the extraction of more than 40 elements by trioctylarsine oxide was tested by activation analysis and a detailed study was made of the extraction of iron(III), zinc(II), cadmium(II), hafnium(IV), and zinc(IV).[266] The authors' determination for the equilibrium constants for the formation of the zinc and cadmium halide complexes are of great importance for the estimation of the reactivity of the extractant. At the same time it was established that the extraction of hafnium and zirconium differs appreciably from the extraction of the above elements by phosphine oxides. The principal difference consists in the exceptional stability of the ion $(Oct_3AsOH)^+$, formed with the increase of the acid concentration, whose presence in solution sharply reduces the degree of extraction of metal ions[266].

In order to elucidate the nature of the interaction between the extracted metal and trioctylarsine oxide, a study was made by vibrational spectroscopy of the composition of the extracts formed in the extraction of molybdenum(VI) from sulphuric acid solutions. It was shown that trioctylarsine oxide effectively extracts molybdenum(VI) from sulphuric, hydrochloric, and nitric acid solutions. Regardless of the type of acid, the maximum extraction is observed in the pH range 2–3. It has been established[267] that molybdenum(VI) is extracted from sulphate solutions in the form of molybdenum-containing acids. The above data are fully consistent with the results of the study of the extraction of $CoCl_2$ by R_3NO, R_3AsO, and R_3PO solutions in benzene and CCl_4.[66] The effective constant for the extraction of cobalt decreases by five orders of magnitude, regardless of the solvent, on passing from R_3NO, to R_3AsO, and R_3PO.

The possibility of the quantitative extraction of uranyl nitrate was first investigated by Pietch and Nagl[268]. In the study of a solution of TPAO in chloroform they showed that uranyl ions are fully extracted from nitric acid solutions at pH 2–3. The addition of $NaNO_3$ or $Ca(NO_3)_2$ increases the partition coefficient and extends the limits of effective extraction. The use of EDTA in the process permits the selective extraction of uranium[269]. A study was published later in which methods for the selective extraction of iron(III), in particular in the presence of uranium(VI), were considered at a hydrochloric acid concentration ≥ 8 M.[270]

Among the transuranium elements (M^{3+}), a study has been made of the extraction of americium(III), curium(III), and promethium(III) into cyclohexane solutions of trioctylarsine oxide from aqueous solutions with a variable content of nitric acid and lithium nitrate[271]. The similarity of the dependences of the partition coefficients of M^{3+} on the concentrations of HNO_3 and $LiNO_3$ at constant concentrations of trilaurylamine and trioctylarsine oxide as extractants led the authors to the conclusion that the compound extracted is the complex $TOAO.HNO_3$. It has also been established that, in the case investigated, the extraction properties of trioctylarsine oxide differ significantly from those of its phosphorus-containing analogue. In extraction with a mixture of trilaurylamine and trioctylarsine oxide a synergistic effect is observed, its magnitude depending little on the ratio of the extractants and the nature of M^{3+}. When the organoarsenic compound in the above mixture is replaced by the analogous phosphorus-containing ligand, both synergistic and antisynergistic effects are observed.

The extraction of actinides with TAO has been studied in greatest detail[272] in relation to the partition of trace amounts of uranium, plutonium, and neptunium in different oxidation states between aqueous nitric acid solutions and solutions of aliphatic and aromatic arsine oxides in dichloroethane. On the basis of the linear relations between $\overline{K}_{HNO_3}$ and the constants for the extraction of the actinides (An) by trialkylarsine oxides, one should expect in the given reaction series a parallel increase of $\overline{K}_{An}$ with a sharp increase of the extraction constants owing to the transition to an ion-exchange process mechanism. It has been shown[272] that all the tertiary arsine oxides investigated are powerful extractants of transuranium elements and have values of $\overline{K}_{An}$ ranging from 10^8 to 10^{11} depending on the type of ion extracted, its oxidation state, and the structure of the extractant investigated. The extraction constants of the actinides increase in the sequence Pu(IV) < Np(IV) < Np(VI) < U(VI) < Pu(VI), reaching 10^{11} mol^2 litre^{-2} in the extraction of plutonium(VI).

These values exceed by more than three orders of magnitude the constants for the extraction of the actinides by the isomeric phosphine oxides and are among some of the highest of all those known at the present time. The sequences corresponding to the extractability of metals by phosphine oxides and arsine oxides are the same, which is an argument in support of a single mechanism of the extraction of the actinides by the organoelemental extractants R_3EO with E = P or As. The fact that, regardless of the degree of oxidation, the partition coefficients K_D and extraction constants $\overline{K}_{An}$ of all the actinides investigated decrease on substitution of the phenyl groups in the arsine oxide molecule by octyl substituents merits special attention[273].

The quantitative relations between the basicities of a number of TAO with aromatic and aliphatic substituents at the arsenic atom and the constants for the extraction of the actinides from aqueous nitric acid solutions have been investigated[274]. The linear relation between $\overline{K}_{HNO_3}$ and pK_a implies that the partition of protic acids between aqueous and organic phases under standard conditions for the given

series of compounds is determined by the basicity of the arsenyl oxygen and hence can serve as a measure of its electron-donating capacity. On passing from protic to aprotic metal salts, the linear relations between the pK_a of the compounds and the extraction constants persist, but the increase of the basicity of the TAO (in contrast to their phosphorus-containing analogues) is accompanied by a decrease of the extraction capacity in relation to all the actinides investigated.

The attempt to describe the extraction of the actinides in terms of indices of the electron-donating capacity ($K_{HOC_6H_5}$ and ΔH_T°) proved less successful, since the correlation parameters of these equations were somewhat impaired. It has also been established[274] that the values of $\overline{K}$ for HNO_3 and the actinides are linked by linear relations, but, in contrast to the organophosphorus extractants, they vary in opposition, i.e., after the successive substitution of the aryl groups R by alkyl groups, the extraction capacity of R_3AsO increases in the extraction of protic acids and decreases in the extraction of the actinides.

Thus arsenic compounds have specific features which distinguish them from organophosphorus derivatives and are related to the specific features of the electronic and steric structures. Both these factors can give rise to the observed effect, but, in the absence of non-empirical quantum-chemical calculations for arsenic compounds and thermodynamic parameters of the extraction equilibria involving organoarsenic derivatives, one cannot at the present time give preference to any one of the possible explanations. However, the results obtained leave no doubt that the use of organoarsenic extractants in the far-reaching elimination of radioactive and toxic elements from aqueous solutions is promising. It may be hoped that, with expansion of studies using TAO, other applications of this interesting class of organoelemental compounds will be discovered in both analytical and coordination chemistry and in hydrometallurgical sorption-extraction processes.

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Synthesis of Nitrogen-containing Compounds by the Interaction of Nitro-compounds with Carbon Monoxide

V.I.Manov-Yuvenskii and B.K.Nefedov

The methods and catalysts for the synthesis of nitrogen-containing compounds (oximes, Schiff bases, amides, imides, amines, ureas, urethanes, isocyanates, and azo-compounds) by the interaction of nitro-compounds with carbon monoxide are considered. The reaction mechanisms are discussed and the characteristics of the synthesis of mono- and di-isocyanates are noted.
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I. INTRODUCTION

The catalytic interaction of nitro-compounds with carbon monoxide, which is a new and little investigated field of organic catalysis, has become in recent years one of the currently most important fields of industrial organic synthesis. The reason for this is that a whole series of industrially important compounds can be obtained from nitro-compounds and carbon monoxide in a single stage: azo-compounds, amides, amines, oximes, urethanes, ureas, and isocyanates.

The synthesis of oximes by the reduction of aliphatic nitro-compounds with carbon monoxide constitutes a new approach to the solution of the problem of synthesising intermediates in the manufacture of caprolactam. Urethanes and ureas are important final products and intermediates in the synthesis of fertilisers and pesticides and the development of a method of the direct synthesis of these compounds is of undoubted interest.

Aromatic mono- and di-isocyanates are valuable intermediates in the manufacture of pesticides, rigid and elastic polyurethane foam plastic (widely used in building, furniture, refrigeration, and transport industries), synthetic leather, adhesives, and coatings[1-3]. The world production of isocyanates during the period from 1970 to 1975 doubled and according to predictions will continue to grow at the same rate[4]. In the USA the annual increase is 9% and by 1980 the total production based on isocyanates will exceed 1 million tonnes annually[5]. However, the requirement for isocyanates is by no means fully satisfied, since their modern production is based on the obsolete method involving the treatment of amines with phosgene. In the course of the last decade intense research has therefore been prosecuted in order to develop a new and much more economical method of synthesising isocyanates by carbonylating nitro-compounds. The assembly of the first experimental plant is already being completed in Japan and in 1980 it is planned to begin the manufacture of isocyanates by the new method[6].

This review gives a systematic account of the advances in the last 7–10 years in the field of the catalytic synthesis of nitrogen-containing compounds (oximes, Schiff bases, amides, imides, amines, ureas, urethanes, isocyanates, and azo-compounds) by the interaction of CO and nitro-compounds. Attention is concentrated on the catalysts and the process conditions; furthermore the synthetic possibilities of the method involving the carbonylation of nitro-compounds and the prospects for its employment in organic synthesis are demonstrated.

II. THE PRINCIPAL FACTORS INFLUENCING THE INTERACTION OF NITRO-COMPOUNDS WITH CARBON MONOXIDE

When an attempt is made to arrange systematically the reactions of nitro-compounds with CO (see Table), two principal types of interactions can be distinguished: the reduction of nitro-compounds without the addition of CO to the latter and the addition of a CO molecule to the intermediates in the reduction process (carbonylation). The reaction pathway is in many respects determined by both the catalyst and the reaction conditions, on the one hand, and by the nature of the third component, which in most cases plays the role of the reaction medium, on the other.

The interaction of CO with nitro-compounds is a thermodynamically favourable process[7], but in the absence of a catalyst it proceeds with much difficulty. This is probably due to the high activation energy for the reaction with the reactants being readily activated when adsorbed on the catalyst.

By varying the nature of the catalyst, the reaction medium, and the reaction conditions (temperature, pressure, and reaction time), it is possible to alter both the reaction pathway and the yield of products and the selectivity of their formation. We shall consider the influence of the principal factors on the interaction of nitro-compounds with carbon monoxide.

Catalyst

Transition metals (as a rule Group VIII metals), copper salts, sulphur, and selenium and its compounds, which are capable of forming complexes with both CO and with the nitro-compound, catalyse the reactions of nitro-compounds with carbon monoxide. In the vast majority of cases the reaction proceeds in the liquid phase in the presence of homogeneous catalysts, although instances of the use of heterogeneous catalysts of analogous composition are known.

Despite the lack of data on the comparative activities of the known catalysts, analysis of the available publications (frequently contradictory) permits the conclusion that best results are obtained using palladium and rhodium compounds. Here one should note that the activity of the same compound is greatly influenced by the type of promoting additive and its amount, the nature of the third component, temperature, and carbon monoxide pressure. Tertiary amines, for example pyridine, quinoline, and their derivatives, quaternary ammonium salts, phenylphosphines, and salts of Group IIB, V, VI, and VIII transition metals, particularly vanadium, molybdenum, tungsten, copper, and iron, as well as lanthanide compounds can be used as activators of the palladium and rhodium catalysts.

Synthesis of nitrogen-containing compounds by the catalytic interaction of nitro-compounds with carbon monoxide.

Catalyst	Third component	t, °C	p, atm	Reaction product
—	—	250	3000	Azobenzene
$Fe(CO)_5$	—	200	100—200	Azo-compounds, amines
$Fe(CO)_5$	H_2	160	200	Amines
$Fe(CO)_5$	CH_3COOH	310	100	Acetanilide
$Ni(CO)_4$	CH_3COOH	310	100	Acetanilide
$Co_2(CO)_8$	CH_3COOH	310	100	Acetanilide
$Co_2(CO)_8$	—	190	200	Isocyanates
Copper salts*	—	85	1	Oximes, amines
Copper salts*	Piperidine	20	1	Ureas
Pd**	H_2	200	20	Ureas
Pd**	Alcohols	160	100	Urethanes
Pd**	—	200	900	Isocyanates
$PdCl_2$***	Amines	90	1	Ureas
$PdCl_2$***	Alcohols	150	100	Urethanes
$PdCl_2$***	—	150—200	50—100	Isocyanates
$RhCl_3$***	Water	150	50—120	Amines
$RhCl_3$***	Amines	190	205	Ureas
$RhCl_3$***	Alcohols	150	100—400	Urethanes
	—	120—200	1—300	Isocyanates
$Rh_6(CO)_{16}$****	Aldehydes	170	150	Schiff bases
$Rh_6(CO)_{16}$****	Dialdehyde	170	150	Acid amides
$Rh_6(CO)_{16}$****	Phthalic anhydride Acids and diphenylacetylene	170	120	Acid imides
$Rh_6(CO)_{16}$****	Water	150	50—120	Amines
$Rh_6(CO)_{16}$****	H_2	150—200	100—200	Ureas
$Rh_6(CO)_{16}$****	Alcohols	170	150	Urethanes
$Ru_3(CO)_{12}$	H_2	160	200	Amines, ureas
Se and its compounds	Alcohols	170	50	Urethanes

*In aqueous solutions of highly basic amines.
** On a carrier with added $FeCl_3$ and (or) pyridine.
*** With activating additives.
**** In pyridine.

The reduction and carbonylation reactions of nitro-compounds can also proceed stoichiometrically under mild conditions if CO is first bound in active carbonyl complexes, for example of the type of $Fe(CO)_5$ or iron acyl carbonyls.

Temperature

The process temperature is selected depending on the catalyst employed, the third component, and the CO pressure. For example, in the presence of $PdCl_2$ as the catalyst and activators, the carbonylation of nitro-compounds to give substituted ureas in solution in amines proceeds at 90 °C and atmospheric pressure; in order to synthesise isocyanates in an inert solvent or urethanes in alcohols, a temperature of 150—200° and a pressure of 50—100 atm are required. When $RhCl_3$ is employed as the catalyst in the presence of promoting agents, amines are formed at 150 °C (50—120 atm), ureas at 190 °C (200 atm), isocyanates at 120—200 °C (up to 300 atm), and urethanes at 150—230 °C (100—400 atm).

The process temperature influences in its turn both the degree of conversion of the initial nitro-compounds and the selectivity of its transformation. In the general case one should note that, in order to obtain practically acceptable yields of the desired product with a sufficiently high selectivity, the reaction must be performed at 100—200 °C under an increased CO pressure. At a lower temperature the rate of reaction is low, while an increase of temperature above 200 °C as a rule leads to undesirable side reactions, in particular to tar formation, which lowers the selectivity and deactivates the catalyst.

Carbon Monoxide Pressure

The working pressure depends on the nature of the nitro-compound, the catalyst, the third component, and the temperature. For example, mononitro-compounds are converted into isocyanates at a pressure of 50—100 atm, while, other conditions being equal, the dinitro-compounds require 200 to 300 atm. The reduction of nitro-compounds to amines, azo-compounds, amides, and imides proceeds at a lower pressure than their carbonylation to urethanes or isocyanates, which is apparently associated with the activating effect of the third component on the catalyst.

In addition, an increased CO pressure is necessary to maintain the catalytic complex in an active equilibrium state, which is characteristic of the majority of catalytic reactions of organic compounds involving carbon monoxide and occuring in the presence of carbonyl complexes of transition metals. In the synthesis of isocyanates by the carbonylation of nitro-compounds an increase of pressure (beyond the minimum value required for each catalyst) increases the productivity and makes it possible to reduce the reaction temperature to some extent.

The Third Component

The presence of the third component in the reaction system influences both the reaction pathway and the activity of the catalyst. The third component can be a reactant and (or) the reaction medium. Typical third components which are reactants in the reactions of nitro-compounds with CO are H_2 and aldehydes; hydrogen donors such as water, alcohols, and amines are also used as both the reactant and the reaction medium, while inert solvents, for example, aromatic and aliphatic hydrocarbons, chlorobenzene, or dichlorobenzene are used as inert solvents.

If the nitro-compound reacts with CO in an inert solvent, then mainly isocyanates are formed, two out of the three reacting CO molecules functioning as reductants. In the presence of H_2 in the reaction system, the nitro-compound is as a rule reduced to the amine; sometimes substituted ureas are formed together with the amine, possibly as a result of the carbonylation of the amine formed initially. Aldehydes and hydrogen donors such as amines and alcohols interact either with the catalyst in the complex with the deoxygenation product of the nitro-compound or with the isocyanate formed, giving rise to the corresponding derivatives. Stable compounds, for example, Schiff bases, ureas, and urethanes, can be isolated from the reaction mixture as the products; unstable compounds, for example carbamic acids or their anhydrides, which can be formed in water or acetic acid,

decompose with the evolution of CO_2 and the formation of carboxylic acid amides.

One should bear in mind that the majority of the known third components are effective complex-forming agents. When homogeneous metal-complex catalysts are used, they can therefore enter into the coordination sphere of the transition metal together with the nitro-compound and CO and thereby facilitate or hinder their activation. Consequently the third component can fulfill yet another function: it can regulate the activity and selectivity of the catalyst and can even alter the type of interaction of the nitro-compound with CO.

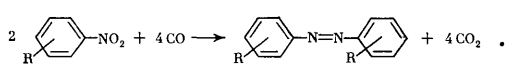
It would be premature to reach a final conclusion concerning the scientific justification of the subdivision of the catalytic reactions of nitro-compounds with CO into reduction without the addition of CO to the nitro-compound and carbonylation, because this new field of organic catalysis has been inadequately investigated. However, this approach permits a more clear-cut estimate of the fundamental achievements in this new field of industrial organic synthesis and a deeper understanding of the mechanism of the reactions of nitro-compounds and CO in the presence of catalysts and also enables one to outline ways of improving and developing the reactions under consideration.

III. REDUCTION OF NITRO-COMPOUNDS

1. Synthesis of Azo-Compounds

The interaction of carbon monoxide with nitro-compounds in the absence of a catalyst proceeds with much difficulty. Thus the conversion of nitrobenzene into azobenzene requires a high carbon monoxide pressure—3000 atm.[8] On the other hand, carbon monoxide bound in a carbonyl complex readily interacts with aromatic nitro-compounds, converting them into azobenzene derivatives[9,10]. The reaction takes place at atmospheric pressure. Under the influence of $Fe(CO)_5$, azobenzene, 2,2′-dimethyl-, 3,3′-dimethyl, and 4,4′-dimethylazobenzenes are formed in 48–76% yields from nitrobenzene and *o*, *m*, and *p*-nitrotoluenes respectively; 1,2-dinitrobenzene is converted to the extent of 11% into 2,2′-diaminoazobenzene.

Iron pentacarbonyl is an active catalyst of the reduction of nitro-compounds with carbon monoxide. In its presence the synthesis of azo-compounds from nitrobenzene and its derivatives takes place at 200 °C and a pressure of 100–200 atm [11]:



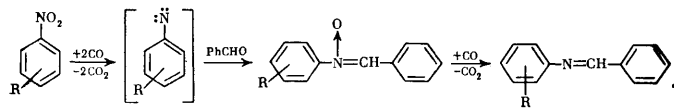
Azoxy-compounds are formed as intermediate. Nitrobenzene is reduced most selectively (the yield of azobenzene is 79%). 4-Chloro- and 4-bromonitrobenzenes are converted into 4,4′-dichloro-, and 4,4′-dibromo-azobenzenes to the extent of 55–56%. Azo-compounds are formed in yields of 18–32% from 4-fluoro- and 4-iodo-nitrobenzenes and in yields of 44–45% from 4-nitrotoluene and 4-nitroanisole[11].

2. Synthesis of Oximes

Nitropropane, nitrobutane, and nitrocyclohexane are reduced quantitatively by carbon monoxide to oximes in aqueous amine solutions of copper salts at 85 °C and atmospheric pressure. The reaction takes place only in the presence of highly basic amines, for example, ethylenediamine. Copper(I) salts are catalytically more active than copper(II) salts. Silver(I) salts are active only at an increased CO pressure, while mercury, cobalt, nickel, and manganese salts do not exhibit catalytic activity in this reaction[12–14].

3. Synthesis of Schiff Bases

The reduction of aromatic nitro-compounds (nitrobenzene, 4-nitroanisole, 4-nitro-*N*,*N*′-dimethylaniline, 2-, 3-, and 4-nitrotoluenes, and 4-nitrobiphenyl) by carbon monoxide under a pressure of 150 atm at 170 °C in the presence of benzaldehyde leads to the formation of Schiff bases in yields of 60–85%.[15] The reaction is catalysed by $Rh_6(CO)_{16}$ in pyridine. It is believed[15,16] that a nitrene is formed from the nitro-compound and CO in the first stage and then reacts with the aldehyde and carbon monoxide to give the final product:

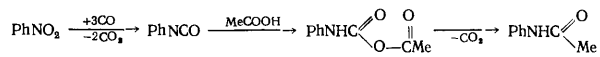


4. Synthesis of Amides and Imides

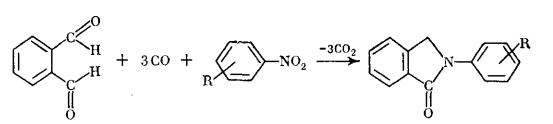
When primary and secondary aliphatic nitro-compounds are heated with iron pentacarbonyl in dry diglyme at 120 °C for 15 h, formamides are formed in low yields (3–20%). On replacing $Fe(CO)_5$ by $Fe_2(CO)_9$, the reaction takes place even at room temperature, but, instead of formamides, the nitrene complexes $(RN)_2Fe_3(CO)_9$, $(RN)_2Fe_2(CO)_6$, and $(RN)_2Fe_2(CO)_7$ are formed from the nitro-compounds and are then converted on heating in diglyme into formamides and urea derivatives[17].

Acetanilide, propionanilide, and benzanilide are obtained in high yields (68–86%) when nitrobenzene interacts with iron acyl carbonyls. The reaction proceeds at room temperature and in an inert atmosphere[18].

Acetanilide can be obtained catalytically in 68% yield from nitrobenzene in acetic acid in the presence of iron, cobalt, or nickel carbonyls at 310 °C and a pressure of 100 atm. With decrease of temperature, the yield of acetanilide falls sharply:



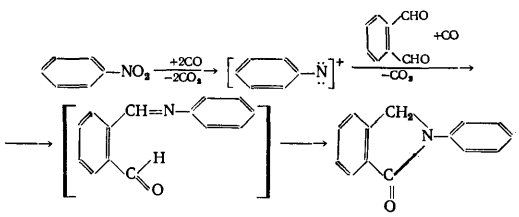
The carbonylation of nitrobenzene with carbon monoxide (150 atm, 170 °C) in the presence of *o*-phthalic aldehyde results in the formation of *N*-phenylisoindolinone[20]. Apart from nitrobenzene, 4-nitroanisole, 3- and 4-nitrotoluenes, and 3-chloronitrobenzene enter into this reaction:



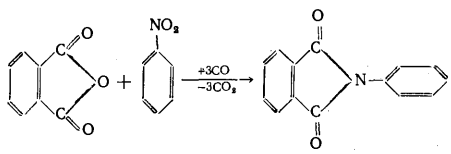
R = H (58%), 4-MeO (42%), 3-Cl (55%), 3-Me (40%), or 4-Me (46%).

The reaction is catalysed by $Rh_6(CO)_{16}$ in pyridine. It apparently proceeds via a stage involving the reduction of the nitro-compound to a nitrene complex, which interacts

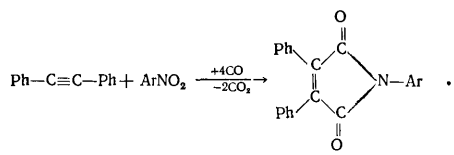
with one aldehyde group to form a Schiff base with subsequent ring closure:



The reduction of nitrobenzene with carbon monoxide (120 atm, 170 °C) in the presence of phthalic anhydride and the same catalyst [$Rh_6(CO)_{16}$ in pyridine] gave *N*-phenylphthalinide in 90% yield[16]:



In the presence of diphenylacetylene, the *N*-phenylimide of 2,3-diphenylmaleic acid is formed under the same conditions in 75% yield[16,21]. 3- and 4-Nitrotoluenes, 3-chloronitrobenzene, and 4-nitroanisole react similarly:



5. Synthesis of Amines

In the synthesis of azo-compounds from 2- or 3-nitrotoluene and $Fe(CO)_5$ in dibutyl ether, small amounts of 2- or 3-toluidine (6–13%) are formed as side products[10]. If the reaction is carried out in methanol which serves as a source of hydrogen, then aromatic amines can be obtained from nitrobenzenes and $Fe_3(CO)_{12}$ in 60–90% yield[22]. In the absence of methanol the reaction stops at the stage where the nitrene complex $(PhN)_2Fe_3(CO)_9$ is formed. The nitro-group is reduced both as a result of the oxidation of carbon monoxide to the dioxide; and as a result of the partial oxidation of iron. The reaction is undergone by 2- and 4-nitrotoluenes, 2- and 4-chloronitrobenzenes, 2-bromonitrobenzene, 1,3-dinitrobenzene, 3-nitroaniline, 4-nitrophenol, 4-nitroanisole, etc.[22]. In aqueous alkaline solutions 4-nitrotoluene, 4-chloronitrobenzene, 4-nitroanisole, and 4-acetoxynitrobenzene are also reduced to the amines under the influence of $Fe_3(CO)_{12}$ (yield 60–92%).

Nitro-compounds are reduced catalytically with carbon monoxide to amines using $Rh_6(CO)_{16}$, $[Rh(CO)_2Cl]_2$, Rh_2O_3, $RhCl_3$, $Ru_3(CO)_{12}$, $Fe(CO)_5$, and copper salts as catalysts.

In the reduction of 4-nitroaniline, 4-nitrophenol, α-nitronaphthalene, and 2-ethylnitrobenzene by carbon monoxide in the presence of $Fe(CO)_5$ in benzene (100–200 atm, 200 °C) the yield of amines is low (less than 30%)[11]. The addition of hydrogen to carbon monoxide to give proportions of 1:1 does not increase the yield. In the presence of $Ru_3(CO)_{12}$ the reaction of nitrobenzene is more selective: at 160 °C and a pressure of 200 atm of the 1:1 $CO + H_2$ mixture the yield of aniline reaches 66%; the yield falls with decrease of the hydrogen concentration[24]. Up to 85–95% of aniline is formed in the reduction of nitrobenzene in the presence of rhodium compounds [$RhCl_3, Rh_6(CO)_{16}$, etc] at 150 °C and a CO pressure in the range 50–120 atm in aqueous pyridine or *N*-methylpyrrolidine[25]. In methanol the reaction proceeds less effectively—the yield of aniline does not exceed 25%. It has been shown[26] that, when copper salts are used as catalysts, nitrobenzene, 2-nitroanisole, 2-chloronitrobenzene, 4-nitrobenzoic acid, and nitromethane are reduced only in highly basic amines containing water. The reduction of nitrobenzene with carbon monoxide to aniline (1 atm CO, 85 °C) takes place to the extent of 50% in aqueous ethylenediamine, 16% in aqueous 1,2- or 1,3-propylenediamine, and 30% in aqueous NH_4OH. The rate of reduction of nitrobenzene increases with increase of the concentration of the copper salt[26].

IV. CARBONYLATION OF NITRO-COMPOUNDS

1. Synthesis of Ureas

The formation of substituted ureas has been frequently observed in the carbonylation of nitro-compounds. For example, prolonged heating of nitroparaffins with a stoichiometric amount of $Fe(CO)_5$ at 130 °C results in the formation of up to 20% of ureas[17]. Diphenylurea has been synthesised in 86% yield by carbonylating nitrobenzene in an aqueous solution at 200 °C and a CO pressure of 70 atm in the presence of SCO.[27] When nitrobenzene, 4-nitroanisole, 4-chloronitrobenzene, 4-nitrotoluene, and nitrocyclohexane were allowed to react with $Fe(CO)_5$ and phenylmagnesium bromide at 0 °C and in an inert gas atmosphere, the corresponding symmetrical *N,N'*-substituted ureas were obtained in yields of 60–99%.[28] *N,N*-Dimethyl-*N'*-phenylurea was synthesised in 86% yield from nitrobenzene and $Me_2NCOSNHMe$ at atmospheric CO pressure[29].

Substituted ureas can also be obtained by the catalytic carbonylation of nitro-compounds. Thus in the presence of $Rh_6(CO)_{16}$ as the catalyst in pyridine, nitrobenzene, 3- and 4-nitrotoluenes, and 4-nitrobiphenyl are converted into the corresponding symmetrical ureas in 70–80% yield at 150–200 °C and a pressure of 100–200 atm under the influence of the 25:1 $CO + H_2$ mixture[16]:

$$2ArNO_2 + 5CO + H_2 \rightarrow ArNHCONHAr + 4CO_2 .$$

When $Ru_3(CO)_{12}$ was used as the catalyst, the highest yield (54%) of *N,N'*-diphenylurea was obtained for the ratio of $CO : H_2 = 9 : 1$, the yield of urea decreasing with increase of the H_2 concentration[24]. Up to 80% of *N,N'*-diphenylurea is formed from nitrobenzene under the influence of the 10:1 $CO + H_2$ mixture in the presence of the 0.5% Pd/Al_2O_3-$FeCl_3$ catalyst[30]. The carbonylation of nitrobenzene in piperidine led to the isolation of *N*-pentamethylene-*N'*-phenylurea:

$$PhNO_2 + 5C_5H_{10}NH + 3CO \rightarrow PhNHCONC_5H_{10} + 2C_5H_{10}NCONC_5H_{10} + 2H_2O .$$

The reaction proceeds at atmospheric CO pressure in the presence of copper(I) salts. Nitrobenzene is reduced by piperidine, which is converted into the symmetrical *N,N'*-bispentamethyleneurea[31].

Palladium salts activated by triphenylphosphine and tetraethylammonium chloride permit the synthesis of substituted ureas by the catalytic carbonylation of aromatic nitro-compounds under mild conditions—at 90 °C and atmospheric pressure[32]. *N,N'*-Diphenylurea, *N,N'*-di(4-methylphenyl)urea, and *N,N'*-di(4-chlorophenyl)urea are formed respectively from nitrobenzene in aniline, from 4-nitrotoluene in 4-toluidine, and from 4-chloronitrobenzene in 4-chloroaniline. Carbonylation of 4-chloronitrobenzene in aniline leads to a

mixture of *N*-(4-chlorophenyl)-*N'*-phenylurea, *N,N'*-di(4-chlorophenyl)urea, and *N,N'*-diphenylurea; the carbonylation of the nitro-group may be accompanied by the carbonylation of the C–halogen bond, which leads to the formation of a further two products: the *N*-phenylamide of 4-nitrobenzoic acid and the corresponding urea 4-$PhNHCOC_6H_4NHCONHPh$.[33]

In the presence of $RhCl_3$ the carbonylation of nitrobenzene in aniline takes place at 190 °C and a CO pressure of 205 atm, *N,N'* diphenylurea being formed in 77% yield[34].

2. Synthesis of Urethanes

Urethanes are formed in the carbonylation of aromatic nitro-compounds in alcohols using palladium or rhodium compounds as well as metallic selenium as catalysts. The reaction is carried out for 0.3–20 h under a pressure of 50–400 atm at 150–230 °C:

$$ArNO_2 + 3CO + ROH \rightarrow ArNHCOOR + 2CO_2 \ .$$

In the presence of $RhCl_3$ the products obtained from nitrobenzene and 1-butanol are 4% of n-butyl *N*-phenylcarbamate, 34% of aniline, and 12% of a mixture of butylamines, while nitrobenzene and methanol give rise to 28% of methyl *N*-phenylcarbamate[35]. The addition of metallic iron[36] or $FeCl_3$ [37] to $RhCl_3$ (in proportions of 1:5) increases the yield of methyl *N*-phenylcarbamate to 54 and 81% respectively. The reaction can be carried out in toluene or in an excess of methanol[36,37]. In the presence of the cyclo-octadienylrhodium complex $[C_8H_{12}RhCl]_2$ activated with $FeCl_3$ (1:5), the yield of methyl *N*-phenylcarbamate is 47%.[38]

When $[Rh(CO)_2Cl]_2$ with added iron or copper chloride was used as the catalyst, phenyl *N*-phenylcarbamate was synthesised in 28% yield in phenol, in 1-butanol the product was n-butyl *N*-phenylcarbamate (82% yield), in methanol the product was methyl *N*-phenylcarbamate, while 1,3-dinitrobenzene in methanol gave rise to dimethyl 1,3-phenylenedicarbamate[39]. Ethyl *N*-phenylcarbamate is formed in a low yield (10%) on carbonylation of an ethanol solution of nitrobenzene containing $Rh_6(CO)_{16}$ and pyridine[15].

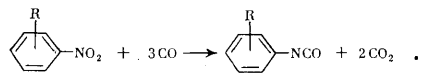
In the presence of the $PdCl_2$–pyridine (1:70) catalyst in ethanol, diethyl 2,4-tolylenedicarbamate was synthesised from 2,4-dinitrotoluene (yield 46–78%), while 1,5-dinitronaphthalene yielded diethyl 1,5-naphthylenedicarbamate. Carbonylation of 2,4-dinitrotoluene in phenol, pentyl alcohol, or ethylene glycol led to diphenyl or dipentyl 2,4-tolylenedicarbamate and ethylene 2,4-tolylenedicarbamate respectively[42–44]. The $Me(COO)_2Pd$–pyridine, $HRh(CO)(PPh_3)_3$, and PtO–pyridine catalysts are less effective.

In the presence of the 5% Pd/C and 5% Pd/Al_2O_3 heterogeneous catalysts activated with $FeCl_3$ carbonylation of nitrobenzene in methanol and of 2,4-dinitrotoluene in ethanol led to the synthesis of methyl *N*-phenylcarbamate (50%) [37] and diethyl 2,4-tolylenedicarbamate (89%) respectively[43,44]. In the presence of pyridine these catalysts are stable and can be used 10–16 times[45]. The analogous rhodium and ruthenium catalysts are less effective than the palladium catalysts (the yield of diurethane is 8–11%).[45] Apart from $FeCl_3$, copper and aluminium chlorides and copper bromide can be used as promoting agents. The carbonylation of ethanol solutions of nitrobenzene, 4-nitrotoluene, and 2,4-dinitrotoluene in the presence of the 5% Pd/C–$FeCl_3$–pyridine catalyst led to the synthesis of ethyl *N*-phenylcarbamate (yield 93%), ethyl *N*-(4-tolyl)carbamate (yield 92–95%), and diethyl 2,4-tolylenedicarbamate (yield 67–82%) respectively[45].

Selenium catalysts exhibit a high activity and selectivity in the synthesis of urethanes. In the presence of selenium and added aniline, trithylenediamine, diphenylurea, acetic acid, and potassium or sodium acetate, nitrobenzene and 2,4-dinitrotoluene in ethanol were converted into ethyl *N*-phenylcarbamate and diethyl 2,4-tolylenedicarbamate in 91–98% yield. The reaction proceeds rapidly (0.5 h) and under relatively mild conditions (50–70 atm, 170 °C).[46,47]

3. Synthesis of Aromatic Monoisocyanates

In 1967 Hardy and Bennett[48] reported for the first time that the carbonylation of aromatic nitro-compounds (nitrobenzene, 2- and 4-nitrotoluene, 3-chlorobenzene, and 3-trifluoromethylnitrobenzene) in benzene under a CO pressure of 500 atm and 190 °C in the presence of palladium and rhodium catalysts results in the formation of aromatic isocyanates (phenyl isocyanate, 2- and 4-tolyl isocyanates, 3-chlorophenyl isocyanate, and 3-trifluoromethylphenyl isocyanate respectively):



The reaction has a characteristic feature—the yield of the product passes through an extremum as a function of temperature, pressure, reaction time, and the amount of catalyst, which is due to the instability of the isocyanate under the conditions of the synthesis.

The catalyst plays a most important role in the formation of isocyanates from nitro-compounds and CO. A wide search has therefore been carried out for effective reaction catalysts. The following compounds were tested: CoI_2,[49] $Co_2(CO)_8$,[50–53] PdO,[54] $PdCl_2$,[55] $RhCl_3$,[56] $PdCl_2 + RhCl_3$ mixture[57], $Pd(PPh_3)_3.Cl_3$,[56] $Pd(C_5H_5N)_2Cl_3$, $Pd(quinoline)_2Cl_2$, $Pd(3,5\text{-dimethylpyridine})_2Cl_2$, and other pyridine complexes of palladium[58], as well as palladium, rhodium or ruthenium on a carrier (Al_2O_3, activated charcoal, $CaCO_3$, pumice, and $BaSO_4$).[59–63] The highest yields of phenyl isocyanate were obtained in the presence of $Co_2(CO)_8$ (46%), $Rh(PPh_3)_3Cl_3$ (40%), and $Pd(3,5\text{-dimethylpyridine})_2Cl_2$ (63%). Heterogeneous catalysts containing ruthenium, palladium, or rhodium on a carrier as well as the chlorides of these metals and PdO are catalytically relatively ineffective.

The activity of palladium and rhodium compounds increases when inorganic and organic compounds are added. In the carbonylation of nitrobenzene in the presence of $RhCl_3$ with added CoI_2 at 200 °C and a CO pressure of 100 atm, 21% of phenylisocyanate is formed[64]. In the presence of the $RhCl_3$–$CuBr_2$–V_2O_5 catalyst at 190 °C and 125 atm, the yield of the isocyanate is higher (45%), but the catalyst must be treated with carbon monoxide for 1–2 h under a pressure of 210 atm and at a temperature of 190 °C before the reaction[65]. The $PdCl_2$–V_2O_5 catalyst also requires a preliminary activation with carbon monoxide under pressure; In its presence the yield of phenyl isocyanate reaches 78–85% but the productivity of the catalyst is low (3–6 g of the product per gram of $PdCl_2$ per hour)[55]. Without preliminary activation with carbon monoxide, the selectivity of this catalyst is low (the yield of the isocyanate with respect to the reacted nitrobenzene is 58%)[66].

When 5% (relative to the weight of nitrobenzene) of phosphine, thionyl chloride, benzoyl chloride, sulphuryl chloride, or vanadium oxide chloride is introduced into the reaction system, and the $PdCl_2$–V_2O_5 catalyst not activated with carbon monoxide is used (190 °C, 145 atm), the yield of phenyl isocyanate is 45–70%.[66] Up to 68% of phenyl isocyanate is formed in the presence of $RhCl_3$–V_2O_5 with added $COCl_2$ or $POCl_3$.[67] In the presence of an excess of phosgene or thionyl chloride the carbonylation of nitrobenzene on the PdO,

$PdCl_2$, $PdCl_2$–$CoCl_2$, $TiCl_4$ and $SnCl_4$ catalysts under a CO pressure of 110–145 atm for 3–37 h leads to the formation of a mixture of isomers of dichloro- and trichloro-phenyl isocyanates with an overall yield of 10–28% instead of phenyl isocyanate[68]. Chlorophenyl isocyanates are also formed in the vapour-phase carbonylation of nitrobenzene in the presence of the catalyst comprising 5% $PdCl_2$–5% $CuCl_2$ on silicon carbide[69].

It has been suggested that aliphatic and aromatic nitriles, triphenylphosphine, quinoline, pyridine, alkyl and bromo-pyridines, and *N*-methylpyridinium iodide be used as organic activators. Patent data[57,70] concerning the activating effect of nitriles have not been confirmed; in fact the inhibiting effect of these additives has been noted[71]. When triphenyl-phosphine is added to PdO, $PtCl_4$, $RhCl_3$ and $PdCl_2$, the yield of phenyl isocyanate increases by a factor of 1.5–2.5 and amounts to 9–34%.[56,71]. The activity of $PdCl_2$ increases sharply after the introduction of quinoline, pyridine, and ethyl, methyl, dimethyl- and dibromo-pyridines: the degree of conversion of nitrobenzene and the yield of phenyl isocyanate increase by a factor of 4–8.[72] Triethylamine, urotropine, and 2,2-bipyridyl deactivated $PdCl_2$.[71]

The low activity of $PdCl_2$ when it is used without additives is due to the ease of conversion of this salt under the reaction conditions into a catalytically inactive form–the polynuclear carbonyl $[Pd(CO)Cl]_n$ [73,74] which decomposes in the presence of pyridine and is evidently converted into the catalytically active complex of the type $Pd(CO)_x(C_5H_5N)_yCl$:

$$\begin{array}{ccc} PdCl_2 & \xrightarrow{\text{pyridine}} & Pd(C_5H_5N)_2Cl_2 \\ \downarrow CO & & \downarrow CO \\ [Pd(CO)Cl]_n & \xrightleftharpoons{\text{pyridine}} & Pd(CO)_x(C_5H_5N)_yCl \end{array}.$$

Indeed the $[Pd(CO)Cl]_n$, which is inactive without additives, makes it possible to obtain phenyl isocyanate in 50% yield and with a nitrobenzene conversion of 64% in the presence of pyridine at 190° and a CO pressure of 100 atm. The $PdCl_2$–pyridine and $Pd(C_5H_5N)_2Cl_2$–pyridine catalysts give rise to similar results under these conditions[50]. When $PdCl_2$ is heated in chlorobenzene containing pyridine, the complex $Pd(C_5H_5N)_2Cl_2$ is formed readily and at an elevated CO pressure is apparently converted into $Pd(CO)_x(NC_5H_5)_yCl$. The catalytically active pyridine palladium carbonyl chloride complexes can be obtained also directly from $PdCl_2$ and pyridine under CO pressure[75].

Complexes having the general formula PdL_2Cl_2 [58] (L = pyridine and quinoline derivatives) are active in the synthesis of phenyl isocyanate and can be arranged in the following sequence in terms of the yield of the isocyanate: Pd(3,5-dimethylpyridine)$_2Cl_2$ (63%) >Pd(4-methylpyridine)$_2Cl_2$ (45%) >Pd(4-ethylpyridine)$_2Cl_2$ (38%) >Pd(pyridine)$_2Cl_2$ (28%) >Pd(2-methylpyridine)$_2Cl_2$ (16%) >Pd(2,3-dimethylpyridine)$_2Cl_2$ (11%) > Pd(quinoline)$_2Cl_2$ (10%) >Pd(2-methylquinoline)$_2Cl_2$ (5%) > Pd(2-ethylpyridine)$_2Cl_2$ (4%) >Pd(3,5-dibromopyridine)$_2Cl_2$ (0%), Pd(2,2-bipyridyl)Cl_2 (0%).

Electron-donating alkyl substituents in the β- and γ-positions in the ligand of this complex increase and those in the α-position decrease the degree of conversion of nitrobenzene and the yield of phenyl isocyanate. In the presence of palladium complexes with ligands more bulky than pyridine (quinoline and 2-methylquinoline) the yields of isocyanate are lower by factors of 2.8 and 5.6 respectively. When an electron-accepting substituent, for example, bromine, is introduced in the β-position of the pyridine ligand, nitrobenzene is not carbonylated.

Bulky substituents in the α-position of the pyridine ring should reduce, like electron-accepting substituents, the capacity for coordination, the former due to steric hindrance and the latter due to the decrease of the electron density at the nitrogen atom. Evidently equilibrium is established under carbonylation conditions between the catalytically active pyridinepalladium carbonyl chloride complexes and the inactive $[Pd(CO)Cl]_n$; the greater the capacity of the ligand for coordination to palladium, the greater the displacement of the equilibrium in the direction of the active complexes, and the higher the degree of conversion of the nitrobenzene and the yield of phenyl isocyanate. The introduction of an excess of the free ligand into the reaction mixture should also increase the amount of the catalytically active complexes and hence the degree of conversion of the nitro-compound and the yield of the isocyanate. Indeed the addition of a sevenfold excess of the ligand L to the PdL_2Cl_2 complexes and to the $PdCl_2$–pyridine system (molar ratio 1:2) increases their activity[58,71]. Under these conditions, the effect of the excess ligand is manifested particularly sharply for complexes which give rise to a small yield of the isocyanate in the absence of the free ligand. Thus the yield of phenyl isocyanate in the presence of the complexes Pd(2-ethylpyridine)$_2$.Cl_2, Pd(quinoline)$_2Cl_2$, and Pd(pyridine)$_2Cl_2$ increases by factors of 14, 4, and 1.7 following the addition of the corresponding ligand, while in the case of the complex Pd(3,5-dibromopyridine)$_2Cl_2$ the yield increases from 0% to 50%. The addition of the excess ligand to the palladium complexes with 4-methyl, 4-ethyl, and 3,5-dimethyl-pyridines results in an increase of the yield of phenyl isocyanate only by a factor of 1.1–1.6.[58]

2,2′-Bipyridyl forms stable chelate complexes which are evidently incapable of being converted into catalytically active complexes under the influence of carbon monoxide. The addition of 2,2′-bipyridyl therefore not only does not activate the complex Pd(2,2′-bipyridyl)Cl_2,[58] but actually fully deactivates $PdCl_2$ and the $PdCl_2$–pyridine catalyst[71].

The activity of $PdCl_2$ increases sharply in the presence of *N*-methylpyridinium iodide or the pyridine–MeI mixture capable of forming a salt[76], which makes it possible to synthesise phenyl isocyanate in a high yield (76–90%) at 160 °C and a CO pressure of 100 atm. The promoting effect of *N*-methylpyridinium iodide is evidently based on the formation of complexes preventing the conversion of $PdCl_2$ into the catalytically inactive state $[Pd(CO)Cl]_n$ and on the decomposition of the palladium carbonyl chloride already formed (the effect is similar to that of other ammonium salts)[74].

Among all the known catalysts of the carbonylation of nitrobenzene, the three-component catalysts of the type $PdCl_2$–pyridine–inorganic activator (V_2O_5, V_2O_4, MoO_3, and lanthanide molybdates) are the most active and selective in the synthesis of phenyl isocyanate.

The dependence of the activity of the $PdCl_2$–pyridine–metal oxide catalytic system on the nature of the transition metal oxides has been studied systematically[77] and it has been established that the effect of the oxide of the metal in each transition series of the Periodic System changes consistently: with increase of the number of the Group from III to V and VI, the degree of conversion of nitrobenzene and the yield of phenyl isocyanate increase. The maximum degree of conversion of the nitro-compound and the maximum yield of the isocyanate were obtained in the presence of the oxides V_2O_4 and V_2O_5 [Group (V)]in the first transition series, Nb_2O_5 and MoO_3 (Groups V and VI) in the second transition series, and Ta_2O_5 and WO_3 (Groups V and VI) in the third transition series. With further increase of the number of the Group, the activity in the metal oxide in the

first transition series falls: the degree of conversion of nitrobenzene and the yield of phenyl isocyanate also decrease.

All the metal oxides investigated can be divided into three groups in terms of the activity of the catalyst of the type of $PdCl_2$–pyridine: 1) oxides activating the catalyst (V_2O_4, V_2O_5, MoO_3, and also certain lanthanide molybdates, which increase the rate of carbonylation of nitrobenzene by a factor of 3–4); 2) oxides which do not have an appreciable influence on the activity of the catalyst (Cr_2O_3, Fe_2O_3); 3) oxides which reduce the activity of the catalyst—a large group which includes the remaining transition metal oxides[77,78].

In the presence of the best catalysts, for example $PdCl_2$–pyridine–MoO_3 (or V_2O_5, $La_2O_3.4MoO_3$, $Nd_2O_3.MoO_3$, and $Pr_2O_3.2MoO_3$) the selectivity of the synthesis of phenyl isocyanate at 185–200 °C and a pressure of 100 atm reaches 90–98%.[72,78] These catalysts are active also in the synthesis of substituted phenyl isocyanates: in their presence at 200 °C and a pressure of 100 atm, 2-, 3-, and 4-nitrotoluenes are converted into 2-, 3-, and 4-tolyl isocyanates in yields of 82 to 90% respectively, while 2-, 3-, and 4-chloronitrobenzenes, 3,4-dichloronitrobenzene, and 4-bromonitrobenzene are converted respectively into 2-, 3-, and 4-chlorophenyl isocyanates (yield 70–90%)[74,80–85], 3,4-dichlorophenyl isocyanate (83%), and 4-bromophenyl isocyanate (32%).

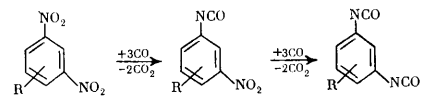
A whole series of monoisocyanates have been synthesised in yields less than 25% by carbonylating 2,4,5- and 2,4,6-trichloronitrobenzenes, 4-fluoronitrobenzene, 3-trifluoromethylnitrobenzene, 2-nitrofuran, 4-nitroanisole, 2-nitronaphthalene, and 5-nitropyrimidine in the presence of $PdCl_2$ and 5% Pd/Al_2O_3 at a high CO pressure (700–1000 atm)[59,61,70,79]. In the absence of activators the palladium catalysts are ineffective at low CO pressures; even in the presence of added activators (pyridine and metal oxides) it is impossible to synthesise isocyanates at atmospheric pressure. A single catalyst, namely $[RhCl(CO)_2]_2$–$MoCl_5$, active in the synthesis of isocyanates at a pressure of 1 atm, is known. Di-, tri-, and tetra-methylphenyl isocyanates are formed in its presence at 120 °C with a low selectivity (less than 50%) from the corresponding nitrobenzenes[86]. Carbonylation is accompanied by the reduction of the nitro-compounds to the amines.

4. Synthesis of Aromatic Di-isocyanates

Group VIII metal compounds have been patented as the main components of catalysts of the synthesis of di-isocyanates by the carbonylation of aromatic dinitro-compounds, but di-isocyanates have been obtained only using catalysts based on palladium and rhodium compounds. Thus the carbonylation of dinitronaphthalene, di(3-nitrophenyl)methane, and di(3-methyl-4-nitrophenyl)methane in the presence of the 5% Pd/Al_2O_3 catalyst results in the formation of a mixture of the corresponding mono- and di-isocyanates[87], while the carbonylation of 1,3-dinitrobenzene in the presence of $PdCl_2$ gives 14% of phenylene 1,3-di-isocyanate[88].

1,3-Phenylene di-isocyanate, 1,4-phenylene di-isocyanate, 2,4-tolylene di-isocyanate, 1,5-dimethyl-2,4-phenylene di-isocyanate, 1,3,5-dimethyl-2,4-phenylene di-isocyanate, and 1,2,4,5-tetramethylene-3,6-phenylene di-isocyanate have been synthesised in yields of 32–75% by the carbonylation of the corresponding 1,3- and 1,4-dinitro-compounds in the presence of the PdO, MoO_3, and Fe_2O_3/Al_2O_3–pyridine catalysts[89]. The yield of the di-isocyanate depends on the relative positions of the nitro-groups in the aromatic ring of the initial compound: di-isocyanates have been obtained from *meta*-dinitro-compounds in yields twice as great as those from *para*-dinitro-compounds.

The synthesis of di-isocyanates proceeds via the intermediate formation of mononitromonoisocyanates, which can be isolated in yields up to 50%:



The yield of di-isocyanates passed through an extremum as a function of temperature, CO pressure, amount of catalyst, and the concentration of the nitro-compound[90,91], which is apparently due to the instability of the di-isocyanates. The optimum conditions for the formation of di-isocyanates in the presence of different catalysts are various: 300 atm and 210 °C for the PdO, Fe_2O_3, and MoO_3/Al_2O_3–pyridine catalysts, 300 atm and 170 °C for the $PdCl_2$–pyridine–Fe_2O_3–MoO_3 catalyst, and 250 atm and 260 °C for the $Pd(pyridine)_2.Cl_2$–Fe_2O_3–V_2O_5 catalyst. Under conditions milder than the optimum conditions, mononitromonoisocyanates are formed, while under more severe conditions tar is produced[90,91].

Among the di-isocyanates, 2,4-tolylene di-isocyanate is of greatest practical importance and the principal data concerning the development of catalysts for the synthesis of di-isocyanates have therefore been obtained for the carbonylation of 2,4-dinitrotoluene. $Co_2(CO)_8$, NiI_2, and $Ni(quinoline)_2I_2$, which have been tested as catalysts of the carbonylation of 2,4-dinitrotoluene with carbon monoxide[92,93], give rise to the mononitromonoisocyanate in a low yield (less than 25%) instead of the di-isocyanate, when $Fe(CO)_5$ is used, isocyanates are not formed at all[10].

At 150–200 °C and a pressure of 175–300 atm the salts $PdCl_2$ and $RhCl_3$ are relatively ineffective in the absence of promoting agents. A number of organic compounds, introduced into the reaction mixture together with the solvent in amounts of 1–10 moles per mole of the catalyst, are used to activate palladium and rhodium chlorides. Compounds such as thiophen, thionaphthene, benzothiophen, dimethyl sulphoxide, diphenyl sulphoxide, sodium sulphite and thiosulphate[94,95], derivatives of furan[96], carbodi-imide[97], aniline[98], formamide and urea[99], cyanamide[100], as well as isocyanates[97], nitroso-compounds[101], and mononitriles[57,70] proved to be relatively ineffective. In their presence less than 10% of 2,4-tolylene di-isocyanate is formed. Activation of $PdCl_2$ by aromatic dinitriles increases the yield to 24%.[102] The best organic activator of $PdCl_2$ is pyridine, whose introduction into the reaction mixture increases the yield of 2,4-tolylene di-isocyanate to 50–68%.[90] Inorganic compounds have a weak activating effect on $PdCl_2$ and $RhCl_3$. Thus, when $PdCl_2$ with added iron, molybdenum, or vanadium oxides, the CuBr–MoO_3 and Fe_2O_3–MoO_3 mixtures, as well as the iron molyb-

dates $Fe_2Mo_7O_{24}$ and $Fe_2(MoO_4)_3$ are used, the yield of di-isocyanates formed from 2,4-dinitrotoluene is 10–20%.[55,65,103] The $PdCl_2$–MoO_3–$CuBr_2$ catalyst subjected to preliminary activation with carbon monoxide in the presence of phosgene makes it possible to obtain up to 40% of 2,4-tolylene di-isocyanate[65]. The attempts to activate palladium and rhodium chlorides with organoelemental derivatives of lead, silicon, germanium, boron, and copper, in the presence of which the yield of di-isocyanate does not exceed 32%, were relatively unsuccessful[54].

The joint use of organic and inorganic activators proved to be the most effective. When chromium, iron, or molybdenum oxides, the Fe_2O_3–MoO_3 mixture, or a mixture of iron (manganese) molybdates is added to the $PdCl_2$–pyridine catalyst, the yield of 2,4-tolylene di-isocyanate is 60%,[104–106] 75%, 85%, 92%, and 73–78%[103] respectively.

Apart from palladium and rhodium chlorides, certain other complexes of the above elements are used as catalysts for the synthesis of 2,4-tolylene di-isocyanates. The complexes $Pd(pyridine)_2(NCS)_2$, $Pd(pyridine)_2(NCO)_2$, $Pd(isoquinoline)_2.(NCS)_2$, $Pd(isoquinoline)_2Cl_2$, and $Rh(pyridine)_3Cl_3$ are relatively inactive without additives; in their presence the yield of the di-isocyanate does not exceed 10%.[107–109]. The complexes of $PdCl_2$ with dimethylcyanamide, dibenzylcyanamide, and diphenylcyanamide made it possible to obtain 4, 5, and 31% of di-isocyanate respectively[100,110]. In the presence of $Pd(pyridine)_2Cl_2$, $Pd(CO)_2Cl_2$, $Pd(CO)(pyridine)Cl_2$, $Pd(CO).(pyridine\ oxide)Cl_2$, $Pd(CO)(2,5\text{-lutidine})_2Cl_2$ and $Pd(CO).(isoquinoline)Cl_2$, 20–40% of 2,4-tolylene di-isocyanate is formed[109,111–114]. It has been suggested that the complexes $Pd(pyridine)_2Cl_2$, $Pd(isoquinoline)_2Cl_2$, and $Rh(pyridine)_3Cl_3$ be activated[108] with hydrogen, water, and formic, oxalic, hydrochloric, and boric acids, which, however, are relatively ineffective (the yield of di-isocyanate is not greater than 44%). Up to 57% of 2,4-tolylene di-isocyanate is obtained in the presence of $Pd(pyridine)_2Cl_2$–MoO_3 to which diphenyl carbonate has been added[115], while in the presence of added diarylurea the yield is only 23%.[116]

One of the most active and selective catalysts of the carbonylation of 2,4-dinitrotoluene with carbon monoxide is the $Pd(pyridine)_2Cl_2$–Fe_2O_3–V_2O_5 system (the yield of di-isocyanate is up to 90%).[117]

Metal chlorides have been tested as activators of the catalyst $Pd(isoquinoline)_2Cl_2$[118]; They can be arranged in the following sequence in terms of the yield of the di-isocyanate: $SbCl_5$ (2%) < $ZnCl_2$ (4–10%) < $PbCl_2$ (11%) < $BiCl_3$ (15%) < $CrCl_3$ (18%) < $MoCl_5$(20%) < VCl_4 (23%) < $TiCl_4$ (25%) < $FeCl_3$ (26%) < $HgCl_2$ (27%) < $ZrCl_4$ (28%) < $MnCl_2$ (32%) < $GeCl_4$ (56%). When Fe_2O_3–CrO_3, CrO_3, or $Cr(CO)_6$–MoO_3 is added to the complex $Pd(isoquinoline)_2Cl_2$, the yield of 2,4-tolylene di-isocyanate increases to 54–65%.[119,120].

The known heterogeneous catalysts of the carbonylation of 2,4-dinitrotoluene are less effective than the homogeneous-heterogeneous catalysts examined above[90,117]. The yield of di-isocyanate on the 9% $RhCl_3/C$-V_2O_5 catalyst in the presence of phosgene does not exceed 29%.[121] The complex $Pd(pyridine)_2Cl_2$ deposited on CrO_3/Al_2O_3 is still less selective (the yield of di-isocyanate is 15%).[122] Not more than 10% of di-isocyanate is formed in the presence of $Pd(pyridine)_2Cl_2$ adsorbed on the copolymer of divinylbenzene, styrene, and 4-vinylpyridine[123,124]. Less than 13% of 2,4-tolylene di-isocyanate has been obtained in the presence of a catalyst containing palladium or rhodium on Al_2O_3, silica gel, activated charcoal[97,125], or $CuBr_2/MoO_3$.[65,126] The heterogeneous catalyst PdO–MoO_3–Fe_2O_3/Al_2O_3 promoted with pyridine exhibits the highest activity and selectivity; in its presence 2,4-tolylene di-isocyanate is formed at a rate of 70 g/g Pd h and with a yield of 70%.[89]

V. THE MECHANISM OF THE TRANSFORMATION OF NITRO-COMPOUNDS UNDER THE INFLUENCE OF CARBON MONOXIDE

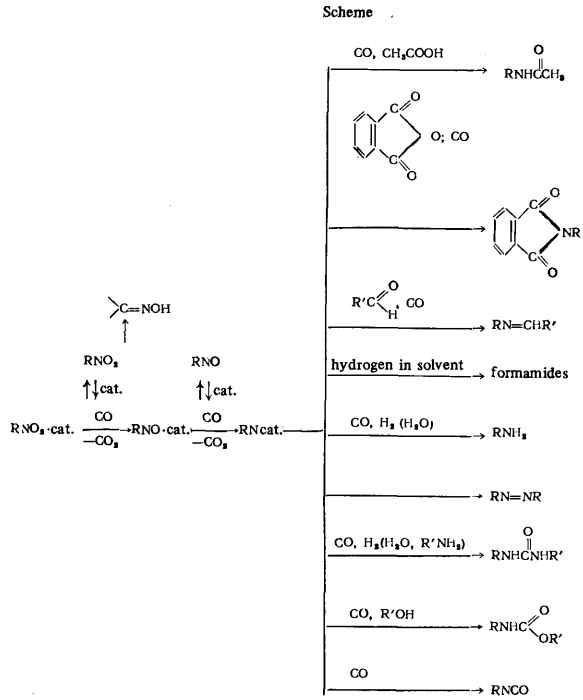
The mechanism of the interaction of CO with nitro-compounds has so far been inadequately studied and it would be premature to reach final conclusions. However, the available data make it possible to formulate a working hypothesis which explains the fundamental features of the process and enables one to outline ways of seeking effective catalysts and new reaction pathways.

In the synthesis of the majority of nitrogen-containing substances (amines, amides, imides, Schiff bases, azo-compounds, substituted ureas, and isocyanates) by the carbonylation of nitro-compounds, one of the intermediates is believed to be a nitrene in a free state or in the form of complexes. Nitrenes are highly reactive short-lived species which exist in the singlet or triplet (biradical) states. The formation of nitrenes is usually inferred from the final reaction products, but it is sometimes possible to detect them in the form of unstable complexes. Thus the nitrene complexes $(RN)_2Fe_2(CO)_6$, $(RN)_2Fe_2(CO)_7$, and $(RN)_2Fe_3(CO)_9$ were isolated in the reduction of aliphatic nitro-compounds with iron nonacarbonyl $Fe_2(CO)_9$; on heating they are converted into formamide and ureas[17]. Under the influence of $Fe_3(CO)_{12}$, nitrobenzene also gives rise to the nitrene complex $(RN)_2Fe_3.(CO)_9$, which is converted into aniline in the presence of a source of hydrogen[22].

The catalytic reduction of aromatic nitro-compounds in the presence of $Fe(CO)_5$, leading to the formation of amines and (or) azo-compounds (depending on the reaction conditions and the nature of the nitro-compound), evidently also proceeds via the intermediate formation of nitrene complexes with iron carbonyl. This is indicated by the formation of side products specific to the nitrene mechanism (carbazole, etc.)[11]. An analogy has been established between the catalytic (on $PdCl_2$) carbonylation of nitro-compounds and the reactions of aryl azides (a classical source of nitrenes): the selectivity of the synthesis of isocyanates increases with increase of the CO pressure and identical side products are formed[79,127]. Indirect evidence for the nitrene mechanism has also been obtained in the carbonylation of nitrobenzenes on rhodium catalysts. It was found (see Table) that the reaction pathway depends on the composition of the reaction medium: under identical conditions, in the presence of hydrogen in the gas phase, ureas are formed, in ethanol a mixture of an amine, urea, and urethane is obtained, in the presence of mono- or di-aldehydes Schiff bases and amides are isolated respectively, while in the presence of diphenylacetylene the products are the *N*-arylimides of 2,3-diphenylmaleic acid[15,16,20,21,25].

On the basis of the data available at the present time, the overall mechanism of the carbonylation of nitro-compounds can apparently be represented as follows. Under the influence of the reducing medium (CO), the metal complex catalyst is converted into one of its reduced forms, for example $[HFe(CO)_{11}]$,[23] $[RhCl(CO)_2]_2$,[86] and $Pd(CO)_x(pyridine)_yCl$,[58] and interacts with the nitro-compound and then with the nitroso-compound, forming a charge-transfer complex[86,128], in which an electron is transferred to the nitro-, or nitroso-group. As a result of deoxygenation within the coordination sphere, a nitrene complex is then formed, and depending on the reaction medium, the nature of the central atom, the ligands in the complex, temperature, and CO pressure is converted into the final products (see the Scheme).

Scheme



Thus the catalytic reduction of nitro-compounds by carbon monoxide makes it possible to obtain a whole series of valuable nitrogen-containing products. This field in the chemistry of nitro-compounds is still not adequately investigated, but the results already obtained indicate the great synthetic possibilities of the carbonylation methods. In the first place the development of an industrial method of synthesising isocyanates is at present of practical importance. There is no doubt about the importance of the above reactions for the theory of homogeneous and heterogeneous catalysis and also for nitrene chemistry.

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The Chemistry of Stabilised Sulphonium Ylides

Yu.V.Belkin and N.A.Polezhaeva

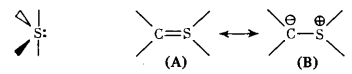
The review is devoted to the chemistry of stabilised sulphonium ylides, i.e. ylides with substituents at the carbanionic carbon atom capable of delocalising its negative charge. The physical properties of compounds of this class are examined and the methods of synthesis of stabilised sulphonium ylides, their rearrangements, and their reactions with electrophiles and nucleophiles are described. The structures and reactivities of the complexes of stabilised sulphonium ylides with transition metals and their organometallic derivatives are considered. The practical applications of the stabilised sulphonium ylides are indicated.
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I. INTRODUCTION

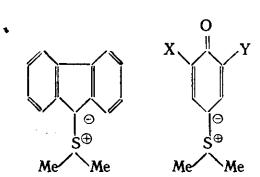
The organic chemistry of sulphur ylides is one of the most vigorously developing branches of organic chemistry. Ylides are compounds in which a negatively charged carbon atom is linked directly to a heteroatom carrying a positive charge[1]. There is at present no systematic nomenclature of sulphur ylides, but the majority of investigators regard them, on Johnson's suggestion[1], as derivatives of the hypothetical sulphurane SH_4. Hence one can consider two classes of sulphuranes: σ-sulphuranes with four σ-bonds and an unshared electron pair, and π-sulphuranes (ylides) having two σ-bonds, one π-bond, and an unshared electron pair. The structure of π-sulphuranes can be described in terms of resonance between ylene (A) and ylide (B) structures:



σ-sulphurane π-sulphurane

In order to avoid ambiguity in the names of σ- and π-sulphuranes, in the present review we shall use the suffix "yl" in the names of the former and the suffix "ylidene" in those of the latter. Thus a substituent containing tetracoordinate sulphur will be referred to as sulphuranyl and one with tricoorindate sulphur will be called sulphuranylidene.

The first representatives of stable σ-sulphuranes having electronegative substituents at the sulphur atom have been obtained recently by Martin and coworkers[2-4]. The first stable π-sulphurane is believed to be dimethylsulphuranylidenefluorene (I),[1,5] which was synthesised[6] approximately 50 years ago. However, there is no doubt that the thioniaquinones (II), synthesised much earlier, belong to this class[7,8]:



(I) (II)

X = Br or NO_2; Y = Br, NO_2, or Me.

Up to the beginning of the 1960's, the chemistry of π-sulphuranes was hardly investigated and this class of compounds became the subject of continued attention by investigators only after the brilliant research of Corey[9] and Franzen[10,11] undertaken in an endeavour to extent the Wittig reaction to sulphur ylides.

At the present time there are a series of reviews in the literature on the chemistry of sulphur ylides[1,4,5,12-25], among which only one has been translated into Russian[1]. However, they are devoted not only to sulphonium ylides, among which attention is concentrated on the non-stabilised ylides, but also to many related compounds, for example sulphoxides, sulphilimines, oxosulphonium ylides, sulphenes, sulphines, etc., which made it impossible to cover sufficiently fully the chemistry of sulphonium ylides.

This review is devoted to the chemistry of stabilised sulphonium ylides, i.e. ylides containing electronegative substituents at the carbanionic carbon atom capable of delocalising its negative charge. The decrease of the nucleophilicity of the carbanionic carbon atom in ylides leads to an appreciable alteration of their chemical properties compared with unstabilised sulphonium ylides, which makes it possible to regard the chemistry of stabilised sulphonium ylides as an entirely independent branch of organic chemistry.

II. PHYSICAL PROPERTIES

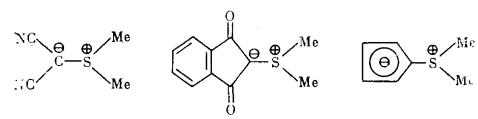
The main question to which investigators turned their attention in the study of the physical properties of sulphonium ylides was that of the nature of the ylide linkage. Initially the majority of investigators assumed that the *d* orbitals of sulphur are effectively involved in the stabilisation of the negative charge on the carbanion via $p_\pi-d_\pi$ bonding[1,18,19] and it was believed that the $p_\pi-d_\pi$ bonding is favoured by the presence of a positive charge on the sulphur atom of the ylide or of strongly electron-accepting substituents linked to the sulphur atom or the α-carbon atom[26-28]. In relation to the simplest sulphonium ylide SH_2CH_2, the problem of the involvement of the 3*d* orbital of sulphur in the formation of the C–S ylide linkage has been recently examined. Using the Hartree–Fock molecular orbital method, it was

concluded that the use of *d* orbitals for the formation of the highest occupied molecular orbital of the ylide results in an appreciable energy gain. Furthermore, the involvement of the *d* orbitals in the formation of the C–S ylide linkage is confirmed, according to the authors[29], by the distribution of charges in the ylide molecule. These data are analogous to those obtained earlier for phosphorus ylides[30].

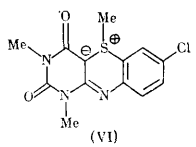
Studies[5,31–34] in which the involvement of the *d* orbitals of Third Period elements (P, S, and Si) is questioned or rejected have been published in recent years. The differences between the properties of the phosphorus, sulphur, and silicon compounds, on the one hand, and those of their analogues in the Second Period, on the other, are explained by the difference between the effective dimensions of their *s* and *p* orbitals[31], the accessibility of the low-lying π^* orbitals of the phosphonium and sulphonium cations[32], or the possibility of the expansion of the valence shell of the heteroatom only as a result of the combination of *s*- and *p*-type orbitals [33,34].

Thus the question of the involvement of the *d* orbitals of the Third Period heteroatoms in the formation of bonds and in particular of the C–S ylide linkage remains open at present.

The physical properties of stabilised sulphonium ylides have been studied very thoroughly. Thus the molecular structure of dimethylsulphuranylidenedicyanomethane (III), [35,36] 2-dimethylsulphuranylideneindan-1,3-dione (IV),[37] dimethylsulphuranylidenecyclopentadiene (V),[38] and 7-chloro-1,3,5-trimethyl-5*H*-pyrimido(5,4-*b*[[1,4]benzothiazine-2,4-[1*H*,3*H*]dione (VI) [39] have been established on the basis of X-ray diffraction data:



(III) (IV) (V)



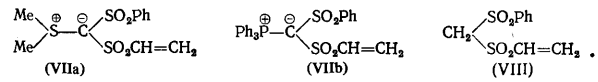
(VI)

The sulphur atom in ylides is pyramidal and the length of the C–S ylide bond (1.71–1.72 Å) is smaller than that of a single C–S bond (1.809 Å) [19] and close to that of the C–S bond in ethylenethiourea (1.708 Å), in which the amount of double bond character has been estimated as approximately 20%.[39] It is noteworthy that in sulphonium salts, where the negative charge is concentrated on the anion, the lengths of all the C–S bonds are close to that of a standard single bond[38]. The bonds between the carbanionic carbon atom and the neighbouring carbon atoms are shortened (1.40–1.43 Å) and the C–O bonds of the carbonyl groups attached to the carbanionic carbon are lengthened (1.23–1.24 Å), compared with the usual values for the C–C and C–O bonds[19,39,40]. In the case of the ylide (V) the distribution of bond lengths in the cyclopentadiene ring approaches the equalised distribution and resembles that in the structure of the analogous phosphorus ylide, for which the proportions of the ylide (~80%) and ylene (~20%) structures have been estimated[38]. The ratio of the latter in the sulphonium ylide is approximately the same, which has been confirmed by ^{13}C NMR spectra obtained recently for the corresponding sulphonium and phosphonium ylides[41].

It follows from X-ray diffraction data that the sulphonium and electron-accepting groups at the carbanionic carbon atom are involved in the delocalisation of its negative charge.

This is also reflected in the infrared spectra of the sulphonium ylides, where in the case of the carbonyl-,[35,42,43] cyano-,[35,44] sulphonyl-,[45] phosphoryl-,[46] and nitro-stabilised[47] sulphonium ylides the stretching vibration bands in these groups are displaced towards lower frequencies compared with the corresponding sulphonium salts[35,42,44,45] and other carbonyl, nitryl, sulphonyl, phosphoryl, and nitro-compounds[48], which is similar to the situation observed for phosphorus ylides[1].

The ultraviolet spectra of the dimethylsulphuranylidene derivatives (VIIa) and the triphenylphosphoranylidene derivatives (VIIb) of benzenesulphonylethylenesulphonylmethane[44] show a broadening of the phenyl band of the ylides and a smoothing of its fine structure compared with the initial methylene compound (VIII):



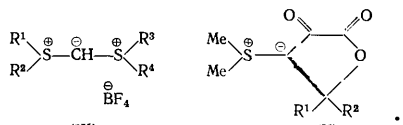
(VIIa) (VIIb) (VIII)

This is evidence for a relatively high electron density on the carbanion in ylides, i.e. ylides exist predominantly in the ylide form (B). Analysis of the ultraviolet spectrum and calculation of the energies of the transitions of dimethylsulphuranylidenecyclopentadiene (V) showed[49,50] that the ylide structure (B) makes an 83% contribution to the ground state and that the latter is stabilised relative to the ylene structure (A) by 1.038 eV (24 kcal). Analogous data were obtained in other studies[51–53]. The ultraviolet spectra of carbonyl-stabilised sulphonium ylides exhibit an absorption which is similar, in terms of the intensity and position of the bands, to that of the enolic form of the corresponding methylene compound but differs appreciably from the absorption of the corresponding sodium salts of the enolic forms[43].

The charge distribution in sulphonium ylides can be inferred from data obtained by the dipole moment method, which are available for the sulphuranylidene derivatives of dicyanomethane[35,54], indan-1,3-dione[54], fluorene[1], and cyclopentadiene derivatives[53,55]. The high dipole moment (4–8 D) shows that the charges in the sulphonium ylides are appreciably separated. However, the dipole moments of ylides are smaller than the value calculated for the ylide structure (B),[1] i.e. the ylene structure (A) makes an appreciable contribution to the ylide–ylene resonance. The dipole moment of the ylide depends on the nature of the substituent at the sulphur atom. Thus replacement of an alkyl group at the sulphur atom by the phenyl group increases the dipole moment of the ylide by 0.4–0.8 D.[54] The introcution of a methoxy-group in the *para*-position of the *S*-phenyl group of the methylphenylsulphuranylidene derivatives of indan-1,3-dione and dicyanomethane increases the dipole moment of the ylide relative to that of the unsubstituted analogue and the introduction of a halogen or the acetyl group lowers the dipole moment of the ylide[54], which indicates the polarity of and ready polarisability of the ylide linkage. In contrast to the data presented above, in their study of the dipole moments of sulphonium, phosphonium, and arsonium ylides derived from cyclopentadienes, Lumbroso et al.[55] concluded that the ylene structure (A) predominates in these compounds.

NMR data are important for the understanding of the geometry and electronic interactions in sulphonium ylides. The positive charge on the sulphur atom leads to the deshielding of the substituent linked to it[42,43,56–58]. The asymmetry of the tetrahedral sulphur atom is responsible for the non-equivalence of the methylene protons of the benzyl or ethyl substituents, which depends on the nature of the solvent[43,59–61], as has been noted for sulphonium salts

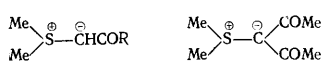
and many other sulphur compounds[62]. In the dimethylsulphuranylidene derivatives of acetophenone and β-dicarbonyl compounds the non-equivalence of the protons of the *S*-methyl groups is not observed even at −60 °C,[59] which can probably be accounted for by the ease of inversion at the sulphur atom. Hindrance of the pyramidal inversion at the sulphur atom should lead to the non-equivalence of the *S*-methyl groups, which has been demonstrated recently for a series of 1,3-bis-sulphonium ylides (IX) in the temperature range 40–80 °C.[63] It was established that the activation energy for this process at 80 °C is 19.8 kcal mol^{-1} and that the barrier to inversion is reduced by approximately 5 kcal mol^{-1} on passing from the salt to the ylide. The non-equivalence of the protons of the *S*-methyl groups can be due to the presence of a chiral centre as the carbanionic carbon atom, which has been observed for the derivatives of 4-dimethylsulphuranylidene-2,3-dioxotetrahydrofuran (X) ($\Delta\delta \cong 0.16$ p.p.m.) and the non-equivalence does not disappear in the temperature range 30–100 °C:[64]



(IX)

(X)

As shown in the study of the molecular structures of the stabilised sulphonium ylides (see above), the bonds between the carbanionic carbon atom and the neighbouring substituents are shortened, so that the existence of rotational isomers may be expected for the stabilised sulphonium ylides. This possibility was demonstrated in an ^{1}H NMR study on dimethylsulphuranylidenemethyl carboxylate (XIa) [58] and dimethylsulphuranylideneacetylacetone (XII),[59] where the non-equivalence of the protons of the methylidyne and *C*-methyl groups was observed as the temperature was altered. The presence of such isomers of dimethylsulphuranylideneacetophenone (XIb) was demonstrated chemically, since its methylation with trimethyloxonium tetrafluoroborate led to the formation of a mixture of the *cis*- and *trans*-vinyl ethers in proportions of 94 : 6:[65]



(XI) (a) R=OMe; (b) R=Ph

(XII)

^{13}C NMR spectra yield extremely valuable information about the reactivities of stabilised sulphonium ylides, their study permitting infereneces about the electronic structure of the carbon atoms in the ylide molecule[41,66–69]. The spin–spin coupling constant of the carbanionic carbon atom with the methylidyne proton in the ylide (XIb) ($J_{^{13}C-H_2} = 179.7$ Hz) confirms that this atom is sp^2-hybridised. The upfield shift of the signal due to the nucleus of the carbonyl carbon atom in carbonyl-stabilised sulphonium ylides relative to the signal of this carbon atom in the corresponding sulphonium salts (−9.5–11.8 p.p.m.) permits the conclusion that the contribution of the ylide structure (B) to the ylene–ylide resonance is important[66]. The substitution of the methylidyne hydrogen atom in the ylide by an electron-accepting substitutent results in a downfield shift of the signal of the carbanionic carbon atom and a reduction of the nucleophilicity of such ylides[66,67].

Important data on the electronic interactions in sulphonium ylides can be obtained by studying the basicity of the latter or the acidity of the corresponding sulphonium salts. Thus the basicity of the sulphuranylidene derivatives of acetophenone decreases after the introduction of electron-accepting substituents in the *para*-position of the S-phenyl or phenacyl group[70,71]. Similar data have been obtained for the phosphonium analogues[72]. The basicity of the sulphonium ylides diminishes in the following sequence of substituents at the sulphur atom: Me > Et > iso-Pr > Ph, i.e. the dialkylsulphonium group is less involved in the delocalisation of the negative charge in the carbanion than the dephenylsulphonium group[73–75]. Thus the introduction of groups stabilising the ylide leads to a decrease of its basicity owing to the greater delocalisation of the negative charge on the carbanion.

The basicity of sulphonium ylides is lower than that of the corresponding phosphonium and ammonium analogues and increases in the sequence S < P < N,[70,71] which depends on the degree of involvement of onium groups in the stabilisation of the carbanionic system of the ylide. The dependence of the stabilising effect of the onium group on the nature of the heteroatom (S ≅ Se ≫ P > As > Sb) has been determined in a study of the ^{1}H NMR and ultraviolet spectra and of the basicities of the corresponding cyclopentadiene ylides[55,75–77]; the analogous series S > P > As > N has been obtained in a study of the rates of isotope exchange of onium salts with D_2O.[78] These data are frequently quoted as evidence for the delocalisation of the negative charge of the carbanion over the *d* orbitals of sulphur[1,55,70], but Kissel et al.[71] regard this as doubtful, since the properties of the ylides examined above can be accounted for also without invoking the "concept of *d* orbitals".

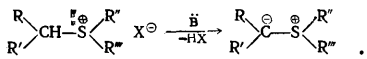
The synthesis of optically active stabilised sulphonium ylides is of great interest. The first attempt at their synthesis was unsuccessful[59], evidently owing to the ease of their racemisation. Theoretical calculation of the barriers to pyramidal inversion and the internal rotation relative to the formally double C=S ylide bond showed that the automerisation of ylides proceeds as a two-stage process[79]. The inversion of the sulphur pyramid is preceded by the rotation about the C–S ylide bond and the *gauche*-conformation constitutes a transition state. The calculated barrier to the inversion of the pyramid at the sulphur atom (35.3 kcal mol^{-1}) corresponds to the condition for its configurational stability; the barrier to rotation about the C–S ylide bond is 8.7 kcal mol^{-1}.[79] Optically active (−)-ethylmethylsulphuranylideneacetophenone has been obtained[80] and it has been shown that it racemises at 90 °C 200 times faster than the corresponding sulphonium salt and approximately 10^{11} times faster than methyl *p*-tolyl sulphoxide. The enthalpy of activation of the ylide is 23.3 kcal, while for sulphonium salts it is 25 to 29 kcal and for sulphoxides 35–43 kcal.[80,81] The greater ease of racemisation of the ylide can be explained by the fact that the interaction of the sulphonium centre with the carbanionic component of the ylide stabilises the transition state for its inversion[80,81]. The fact that the racemisation of the ylide proceeds via the pyramidal inversion mechanism has been confirmed[82]. It was found that the activation volume for this process is close to zero ($\Delta V^{\neq} \cong 0$) in contrast to the t-butylethylmethylsulphonium ion ($\Delta V^{\neq} = +6.4$), whose activation volume corresponds more closely to a transition state involving partial dissociation. A number of optically active sulphonium ylides stabilised by two carbonyl groups were later obtained[83,84].

Thus, stabilised sulphonium ylides are an extremely **unusual class** of organic compounds. They are highly polar **and their stability** is due to the degree of delocalisation of the electron density in the molecule.

III. METHODS OF SYNTHESIS

Several method of synthesising stabilised sulphonium ylides are now known: the "salt method", the "iodonium method", the reaction of sulphides with diazo-compounds, and other less general methods.

The salt method consists in the deprotonation of sulphonium salts already prepared or synthesised *in situ* by means of a suitable base:

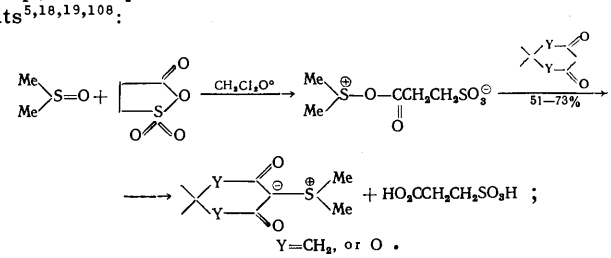


The choice of the base, which can be potassium carbonate, amines, alkoxides, sodium hydride in DMSO, etc.[5,85], is determined by the acidity of the proton at the α-carbon atom of the salt. This method has been used successfully to synthesise a number of carbonyl-stabilised sulphonium ylides[42,86–89]. The applicability of the "salt method" to the synthesis of stabilised sulphonium ylides is limited by the availability of the sulphonium salts and the occurrence of side reactions involving β-elimination and the formation of σ-sulphuranes[5].

The method based on the substitution of the proton at the carbanionic carbon atom of the ylide is a variety of the "salt method". The attempts to alkylate the sulphuranylidene derivatives of acetophenone by methyl iodide, benzyl bromide[42,56,57], and α-halogenoketones[90,91] were unsuccessful, since the reactions were accompanied by the dealkylation of the sulphonium salt formed. The reactions of similar ylides with picryl chloride[92], aromatic amine oxides (*C*-arylation),[93] vinyl ethers (*C*-alkenylation),[94] benzenesulphenyl chloride[95], and *N*,*N*-diethylbenzenesulphenamide[96] (sulphenylation), which led to new stabilised sulphonium ylides, proved more successful.

Carbonyl-stabilised sulphonium ylides can be obtained by acylating ylides with a proton at the carbanionic carbon atom. Acid anhydrides[42,97–99], isocyanates[59,90,99,100], acid azides[101,102], aldehydes, α-diketones, α-ketoacid esters[63], and acyl halides[42,64,95,98,99,103–107] can be used as acylating agents. The employment of acyl halides for the acylation of monocarbonyl-stabilised sulphonium ylides is limited by the formation of *O*-acylation side products, which is evidently associated with the enolate stabilisation of ylides[42].

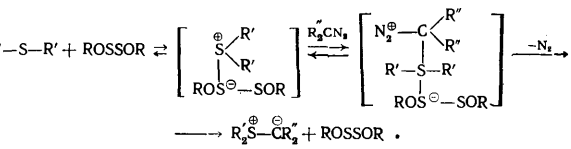
The salt method also includes the condensation of sulphoxides with compounds containing an active methylene group, which proceeds via the intermediate formation of salts[5,18,19,108]:



This reaction takes place under conditions typical for dehydration reactions in the presence of dehydrating agents such as sulphopropionic anhydride[108], acetic anhydride[5,14,18,19] (although in the presence of the latter the yield of the ylide is low owing to the competing Pummerer reaction[109]), phosphorus pentoxide[59], thionyl chloride[59,100], aryl cyanates[111–113], sulphur trioxide[114,115], and dicyclohexylcarbodi-imide[35,52,116,117]. All these reagents form sulphonium salts or complexes with sulphoxides, which readily react with compounds containing an active methylene group. This has been confirmed by the reactions of the stable betaine formed when DMSO reacts with sulphopropionic anhydride[108] and by the reactions of stable sulphonium salts[59,118] with compounds containing an active methylene group or their sodium salts, which led to the formation of the corresponding sulphonium ylides. The yield of the ylide and the rate of its formation when the condensation is carried out in acetic anhydride can be increased by adding to the reaction mixture alkali metal perchlorates, which facilitate the formation of the acyloxysulphonium salt[119]. The reaction of organic selenide dihalides with compounds containing an active methylene group has been used successfully recently to synthesise stabilised selenonium ylides[120]. The attempts to employ this method for the synthesis of sulphonium ylides proved unsuccessful, since the intermediate sulphonium salts readily decomposed with formation of an olefin and an α-halogenocarbonyl compound[121].

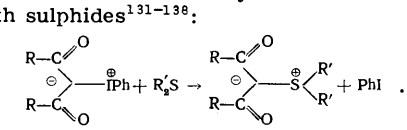
The thermal, photolytic[17,25,66,122–126], or catalytic decomposition[127] of diazo-compounds in the presence of sulphides constitutes a direct method of synthesis of stabilised sulphonium ylides. The reaction evidently proceeds via the nucleophilic attack by the sulphide on the singlet carbene formed on decomposition of the diazo-compound; the high stereoselectivity of this process has been demonstrated[128]. The thermal decomposition of diazo-compounds is usually carried out in the presence of anhydrous copper sulphate or metallic copper powder. This method is applicable to the synthesis of ylides from weakly nucleophilic sulphides such as diaryl sulphides or dibenzothiophen[129]. It is noteworthy that dialkyl sulphides are approximately 4–6 times more reactive in this reaction in relation to the carbene than olefins[126,129].

The catalytic decomposition of diazo-compounds in the presence of sulphides takes place readily at room temperature in the absence of light, provided that dialkoxydisulphides have been added to the reaction mixture[127]; the process probably proceeds via the following mechanism:



The formation of a complex of the sulphide with a dialkoxy disulphide has been observed in the reaction of tetramethylene sulphide with dimethoxy disulphide[127]. In all cases the yield of the ylide decreases with decrease of the nucleophilicity of the sulphide and with increase of the degree of branching of its hydrocarbon groups. Furthermore, the decrease of the yield of the ylide can be caused by the rearrangements and processes involving the cleavage of the ylide under the reaction conditions[17,25,129,130] (see Section IV).

The "iodonium method" of synthesising stabilised sulphonium ylides consists in the transylidation of the iodonium betaines with sulphides[131–138]:



These reactions are catalysed by copper(I) or copper(II) salts[131–135,138] and toluene-*p*-sulphonic acid[136,137]. Although the mechanism of this reaction has not been investigated, when copper salts are used it probably proceeds via the intermediate formation of a carbene or, in the presence of toluene-*p*-sulphonic acid, the intermediate iodonium salt is cleaved by the nucleophilic sulphide at the C–I bond and the resulting sulphonium toluene-*p*-sulphonate is deprotonated further by the counterion, which leads to the corresponding ylide.

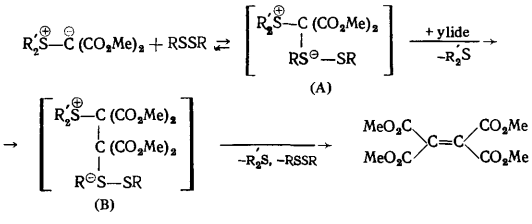
A number of less general methods are also suitable for the synthesis of stabilised sulphonium ylides. Thus ylides can be obtained by the transylidation of other sulphonium ylides in the presence of disulphides activated by electron-accepting groups (dialkoxydisulphides, thiocyanogen, etc.)[139] or electrophilic monosulphides (aryl thiocyanates, *p*-hydroxyphenyl trifluoromethyl sulphide, etc.)[69] as well as by the transylidation of selenonium ylides with sulphides in the presence of carbon disulphide[140]. Stabilised sulphonium ylides can be obtained by adding DMSO to acetylenedicarboxylate[103] or, in the case of the sulphuranylidene derivatives of dicyanomethane, by the interaction of sulphides with tetracyanoepoxyethane[44,110].

IV. CHEMICAL STABILITY. REARRANGEMENTS

It was pointed out above that the stability of sulphonium ylides is determined mainly by the degree of delocalisation of the electron density in their molecules under the influence of electron-accepting substituents.

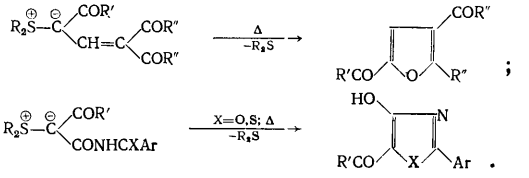
Nothing is so far known about the oxidants on stabilised sulphonium ylides. In a few studies[103,141-143] the reduction reactions have been investigated. When ylides are hydrogenated or are acted upon by sodium hydride, the ylide linkage is cleaved with formation of a sulphide and a hydrocarbon residue. In only one case was the reduction of the carbonyl group without the involvement of the ylide linkage observed[143]. The hydrolytic stability of stabilised sulphonium ylides has been studied in greater detail; it will be examined below in Section VI.

Stabilised sulphonium ylides can be decomposed thermally, photolytically, and catalytically; this very often involves different types of rearrangements. The catalytic decomposition of ylides proceeds readily in the presence of disulphides activated by electron-accepting substituents[144]. Ylides then decompose in the following sequence in terms of the decrease of their reactivity: $R_2\overset{\oplus}{S}-\overset{\ominus}{C}HCOPh > R_2\overset{\oplus}{S}-\overset{\ominus}{C}(\overset{\ominus}{C}O_2Me)_2 \approx R_2\overset{\oplus}{S}-\overset{\ominus}{C}(CN)_2 \gg R_2\overset{\oplus}{S}-\overset{\ominus}{C}(CO_2Me)(COMe)$, which is similar to the series based on the decrease of the nucleophilicity of the carbonionic carbon atom. The decomposition of the ylide, involving its complex with a disulphide, can be represented by the following scheme:



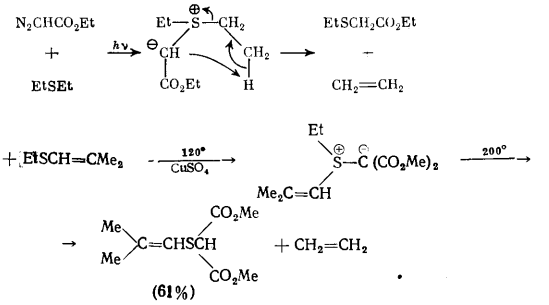
Thus an olefin is formed in the decomposition of the complex (B) obtained as a result of the nucleophilic substitution of the sulphonium group of the complex (A) by another ylide molecule. In the case of highly nucleophilic sulphuranylidene derivatives of acetophenone the olefin formed reacted with the the initial ylide with formation of the corresponding cyclopropane derivatives[144]. The possibility of the formation of cyclopropane derivatives from ylides and olefins has been confirmed by a study of the decomposition of acyldiazo-compounds in the presence of sulphides[144-146].

The thermal and photolytic decomposition of monocarbonyl-stabilised sulphonium ylides leads to the corresponding *trans*-substituted cyclopropane derivatives[18,56-58,98,147-151]. To account for this process, a "carbene" mechanism has been proposed in the case of the photolytic decomposition of the ylide[148,149] and both "carbene" and "ionic" mechanisms have been put forward for the thermal decomposition[56,147-150] and both have been confirmed experimentally: the carbene mechanism by trapping the intermediate carbene with dimethylbenzylamine[56,57], triphenylphosphine[149], cyclohexene[147,148], and other compounds which readily react with carbenes[152] and the ionic mechanism by converting dimethylsulphuranylideneacetophenone (XIb) into *trans*-tribenzoylcyclopropane, the reaction being catalysed by a phenacylsulphonium salt[56,147,150,151]. (For further details of these mechanisms, see Reid[18].) It is noteworthy that sulphonium ylides stabilised by two electron-accepting groups are not converted into cyclopropanes as a result of the low nucleophilicity of the carbanionic carbon atom[144]. However, if one of the stabilising groups is an allyl acetate group or a (thio)carbamoyl group, intramolecular cyclisation of the ylide, leading to furan, oxazole, or thiazole derivatives, becomes possible[100,153]:

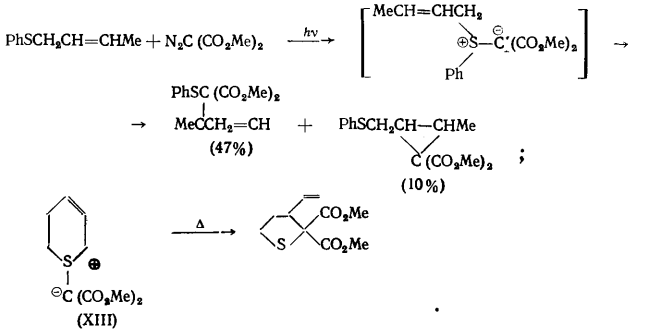


When a substituent with β-hydrogen atoms (ethyl or t-butyl group) is attached to the sulphonium sulphur atom, β-elimination processes are observed instead of conversion into a cyclopropane derivative, which results in the formation of alkyl thioacetates or alkenyl thiomalonates and olefins (Scheme I).[126,154,155] For further details about the β-elimination processes, see Ando[17,25]:

Scheme 1



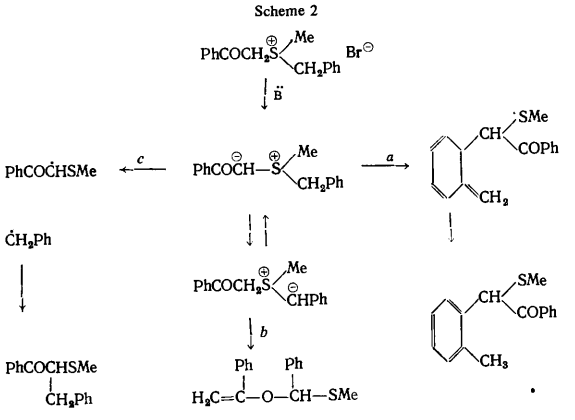
When stabilised sulphonium ylides are decomposed, various rearrangements may occur together with the reactions involving conversion into a cyclopropane derivative, cyclisation, and β-elimination. Thus the thermal or photolytic decomposition of *S*-allyl-substituted sulphonium ylides, including the cyclic ylide (XIII), entails [2,3]-sigmatropic rearrangements leading to the formation of homoallyl sulphides[130,154]:



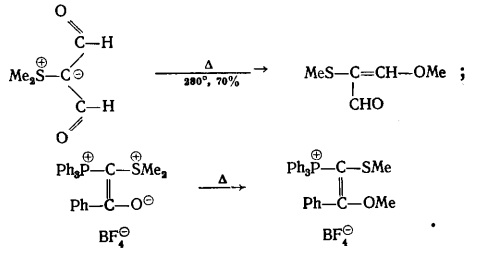
These rearrangements are allowed by the orbital symmetry[156] and occur on heating or photolysis of ylides with complete inversion of the allyl substitutent[130,154]. The method of successive [2,3]-sigmatropic shifts has been used recently in the synthesis of eight- and eleven-membered heterocycles[157]. It is noteworthy that similar [2,3]-sigmatropic rearrangements are observed also for unstable oxonium, ammonium, and halogenonium compounds[130,158].

The Sommelet–Hauser rearrangement, leading to a product substituted in the aromatic ring (pathway *a*),[1,159] and the 1,5-rearrangements of carbonyl- or cyano-stabilised sulphonium ylides, occurring with formation of enolic monothioacetals in the case of carbonyl-stabilised ylides (pathway *b*),[159,160] or keten imines[161], can be included among rearrangements of this type; in the last instance the alkyl group migrates from the sulphur atom to the nitrogen atom of the nitrile group:

Scheme 2

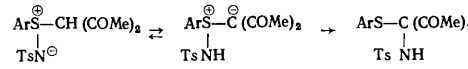


These rearrangements are favoured by a protic solvent, which promotes the proton transfer processes occurring under these conditions. The ratio of the products formed via pathways *a* and *b* depends on the rate of attainment of equilibrium between the two ylide forms and can be controlled by the concentration of a base[159]. The possibility of the 1,5-migration of the alkyl group has been demonstrated not only for monocarbonyl-stabilised sulphonium ylides but also for ylides stabilised by two carbonyl or carbonyl and phosphonium groups[85,162]:

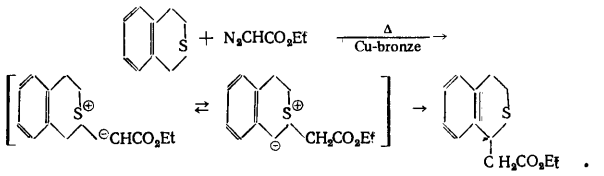


When an aprotic solvent is used, the [1,2]-sigmatropic shift (pathway *c*) of the *S*-alkyl group (the Stevens rearrangement) begins to compete with the above rearrangements (pathways *a* and *b*) and it has been noted that the Stevens rearrangement is favoured by an increase of temperature[159]. Furthermore it has been shown recently for sulphuranylidene derivatives of pyrimido-1,4-benzothiazine[163] that the type of rearrangement depends on the nature of the substituents in the ylide and the reaction conditions (thermolysis or photolysis).

The Stevens rearrangement was discovered in 1932 [164] and consists in the conversion of methylbenzylsulphonium bromide in a methanol solution of sodium methoxide into α-methylthio-β-phenylpropiophenone (evidently via the intermediate formation of an ylide). The concerted mechanism of the thermal Stevens rearrangement is prohibited by orbital symmetry[156], so that the mechanism involving a dissociation–recombination process is more probable. This is confirmed by the finding that the reaction is characterised by a very low value of ρ if the substituents in the benzene ring of the benzyl group are varied[165,166] and by the appearance in the ^{1}H NMR spectrum of benzyl protons of chemically induced dynamic nuclear polarisation[129,165–167]. An interesting example of a 1,2-shift has been observed recently[168] for a new type of sulphonium ylides with an amino-group attached to the sulphonium sulphur atom:

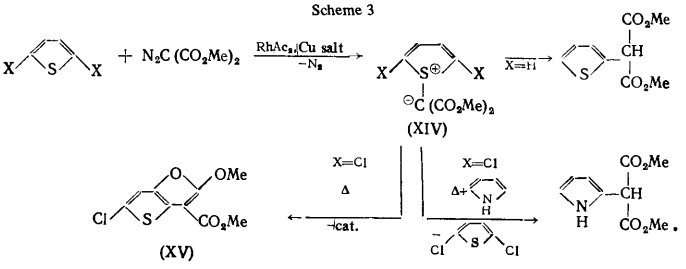


The inclusion of the sulphur atom in a six-membered ring partly makes the 1,2-migration of the *S*-alkyl group energetically unfavourable, since it should occur with formation of a thiepan ring. In this case migration is observed from the methyleneethoxycarbonyl substituent and not the *S*-alkyl substitutent, evidently via an intermediate formation of an unstable ylide[169]:



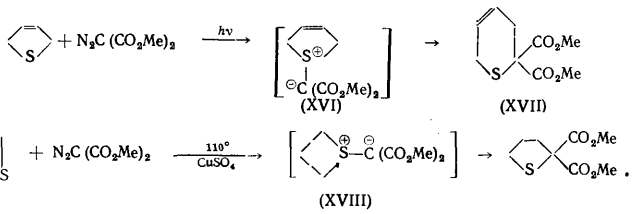
Recently a similar migration of the dimethylmalonate group has been observed in the thermal rearrangement of ylides derived from thiophen occurring on heating them in the presence of rhodium or copper catalysts[170]. Under these conditions, when the α-positions of the thiophen ring are substituted, then in the presence of the above catalysts the ylide dissociates into a sulphide and a carbene; the latter was trapped with activated aromatic compounds (pyrrole, indole, anisole, etc.).[152] It is noteworthy that the ylide (XIV), carefully freed from the catalyst, does not decompose into a sulphide and a carbene but undergoes an intramolecular rearrangement involving the migration of the malonate substituent from the copper atom to the α-position of the thiophen ring with subsequent ring closure, elimination of HCl, and the formation of methyl 5-chloro-2-methoxythieno-[3,2-*b*]furan-3-carboxylate (XV):[171]

Scheme 3



Thus the inclusion of the sulphonium sulphur atom in the ring has a significant effect on the mode of the composition of the ylide. The influence of ring size and the ring substituents on the stability of ylides and the mode of their decomposition can be illustrated by the following examples. Sulphonium ylides obtained from thiophan, tetrahydrothiapyran, thiepan, and dimethyl diazomalonate do not decompose on heating at 235 °C in the course of 10 h.[129] As pointed out above, ylides obtained from derivatives of thiophen

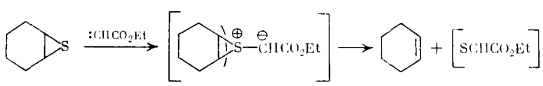
(XIV) or Δ^3-dihydrothiapyran (XIII) and dimethyl diazomalonate behave differently. The former undergoes a 1,2-shift of the malonate group or decomposes into a sulphide and a carbene[152,170,171], while the latter gives rise to products of the [2,3]-sigmatropic rearrangement accompanied by ring contraction[130]. The opposite behaviour has been observed for the ylide (XVI) obtained from 2,5-dihydrothiophen and dimethyl diazomalonate: the Stevens rearrangement, leading to the stable Δ^3-5,5-dimethoxycarbonylthiapyran (XVII) is more favourable than the [2,3]-sigmatropic rearrangement, which leads to the sterically strained thietan[130]:



(XVI) (XVII)

(XVIII)

The sulphonium ylide (XVIII), formed in the reaction of the thietan with dimethyldiazomalonate readily rearranges to 2-dimethylcarbonyltetrahydrothiophen[129]. This process is evidently caused, on the one hand, by the transition of the sulphur from the quadrivalent to the bivalent state and, on the other, by the formation of a less strained five-membered ring. The reactions of ketocarbenes with oxetans proceed similarly[172]. If the sulphur is incorporated in the thi-iran ring, then a stable ylide is also not formed in the reaction of such a sulphide with a carbene. The Stevens rearrangement would lead in this case to a strained thietan, so that α-fragmentation, leading to an olefin and a thiocarbonyl compound, is more favourable under these conditions[173]. Analogous reactions had been observed earlier between carbenes and oxirans[172] and aziridines[174]:



It is noteworthy that the stability of ylides and the mode of their decomposition are influenced also by the nature of the substituents at the carbanionic carbon atom. Thus sulphuranylidene derivatives of dicyanomethane decompose on heating into a sulphide and tetracyanoethylene regardless of the nature of the substituents at the sulphur atom (alkyl, phenyl, tetrahydrothiapyranyl, etc.).[142]

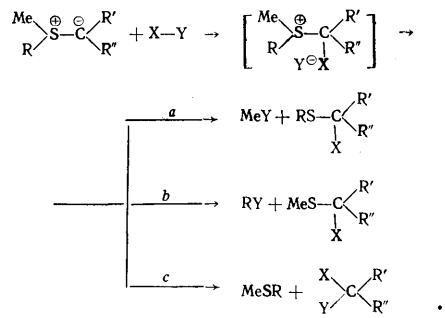
Thus the possibility of the rearrangements must also be taken into account when sulphonium ylides are used in organic synthesis. At the same time the rearrangements of stabilised sulphonium ylides constitute a new method of forming carbon–carbon bonds.

V. REACTIONS WITH ELECTROPHILES

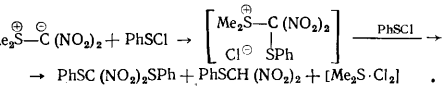
The reactions of stabilised sulphonium ylides with electrophiles are due to the presence of a carbanionic centre in the ylide molecule; with increase of the degree of delocalisation of the negative charge on the carbanion, the reactivity of the ylide with respect to the electrophiles diminishes.

It was started in Section III that one of the main methods of synthesising sulphonium ylides is the "salt method". The reverse reaction involving the regeneration of the sulphonium salt by the addition of hydrogen halides is also possible[13], but the sulphonium salt frequently decomposes under the influence of the nucleophilic counterion in a way which depends both on the substituents in the ylide and on the nature of the nucleophile. A detailed study of these reactions[143,175–179] showed that the sulphonium salts can decompose via three pathways (*a*–*c*). Pathway *a* involves attack by the nucleophilic counterion on the carbon atom of the S–Me group, pathway *b* involves attack on the carbon atom of the S–R group, and pathway *c* involves attack on the carbon atom of the C–X group.

The study of the reactions of dimethylsulphuranylidinedinitromethane with electrophiles (halogens, hydrogen halides, water, sulphuryl chloride, benzenesulphenyl chloride, *N*-halogenoamides, *N*-chloroalkylnitramine, etc.) showed[175–177] that the intermediate sulphonium salt decomposes only via pathway *c*. The formation of products of pathways *a* and *b* is not observed, although this may be caused by their decomposition in the course of the reaction, because it is known that α-polynitroalkyl sulphides are cleaved by both nucleophiles and electrophiles[28,180].



It is noteworthy that the intermediate sulphonium salt can be cleaved not only by the nucleophilic counterion but also by the initial electrophile[176,177]:

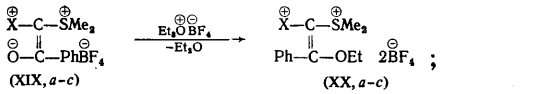


When halogens, sulphuryl chloride, and sulphur monochloride are used in this reaction, competitive halogenation of the *S*-alkyl group takes place[142,176].

In the reactions of sulphuranylidene derivatives of malonic ester with electrophiles (halogens, hydrogen halides, arenesulphenyl thiocyanates, etc.)[178,179] the products of all the above pathways (*a*–*c*) are observed. In the general case the mode of decomposition of the intermediate sulphonium salt depends on the structure of the sulphonium cation (the nature of the groups R and X) and on the nature of the nucleophile. If X is a heteroatomic group, then the substituents at the sulphur atom can be arranged in the following sequence in accordance with the increase of their reactivity with respect to nucleophiles: Me (1.0) ≅ Et (0.6) < iso-Pr (3.0) ≪ CH_2Ph ≅ CH_2SMe (∞). This sequence is different from the sequences based on the reactivity of the substituents in the reactions of alkyl bromides with the bromide anion in acetone at 25 °C: CH_2Ph = Me (1.0) > Et (0.013) > iso-Pr (0.0086), and in reactions of alkylmethylphenylsulphonium perchlorates with the iodide anion in acetone at 50 °C: Me (1.0) > Et (0.20) > n-Pr (0.16) > iso-Pr (0.05),[178] for which the S_N2 mechanism has been established. The higher reactivity of the benzyl and methylthiomethylene groups relative to the methyl group shows that these reactions can proceed via an S_N1 type mechanism[178,179].

In contrast to the reactions of sulphuranylidene derivatives of dinitromethane and malonic ester with electrophiles discussed above, the protonation or alkylation of phenacylide salts (XIX) by acids or triethyloxonium tetrafluoroborate does not take place at the carbanionic carbon atom but

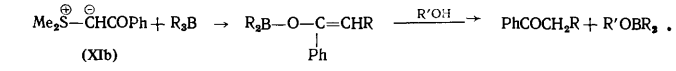
involves the more electronegative end of the carbanionic system—the carbonyl oxygen atom, with formation of the corresponding bis-salts (XX):[162]



(XIX, *a-c*) (XX, *a-c*)

X = (a) Ph_3P, (b) Me_2S, or (c) Ph_2Se.

The reactions of sulphonium ylides with simple electrophiles such as trialkylboranes are of interest[181,182]. The trialkylborane can attack either the carbanionic carbon atom with subsequent C–O rearrangement or directly the oxygen of the enolate form of the ylide, leading to an alkoxydialkylborane after the elimination of the sulphide. It has been established that the alkyl group migrates from the boron atom to the carbon atom in the form of an anion[183]:

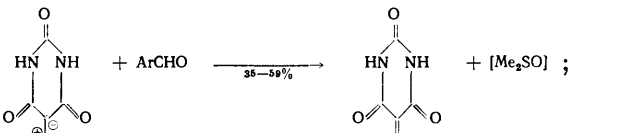


(XIb)

The reactions of sulphonium ylides carrying a proton at the carbanionic carbon atom with acyl halides and alkyl halides have been examined in detail in Section III. Ylides stabilised by two electron-accepting groups also react with them to form sulphonium salts. The structure of the final product is influenced significantly by the nature of the substituents in the sulphonium ion[142,162,184,185]. The reactions of sulphonium ylides with acyl peroxides proceed similarly[186].

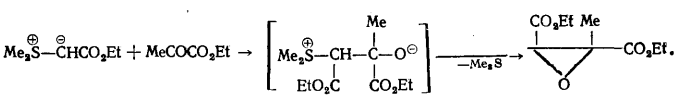
In the study of the chemical properties of stabilised sulphonium ylides much attention was devoted to their reactions with carbonyl compounds and compounds containing multiple bonds[5]. The study of the reactions of ylides with carbonyl compounds was stimulated by the endeavour to extend the Wittig reaction to sulphur ylides. However, instead of the expected olefins, oxirans were obtained in this case. This is probably caused by the lower stability of the S–O bond (E_{diss} = 89 kcal mol^{-1}) compared with the P–O bond (E_{diss} = 128 kcal mol^{-1}) and different tendencies of the sulphide and phosphine groups to be eliminated[1].

The occurrence of the Wittig reaction has been reported in only two instances[187,188]:

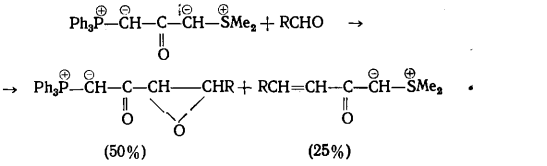


Ar = 4-$Me_2NC_6H_4$, 4-$Et_2NC_6H_4$, or $2O_2NC_6H_4$.

The epoxidation of carbonyl compounds by sulphonium ylides involves the reversible attack by the carbanionic carbon atom of the ylide on the electrophilic carbon atom of the carbonyl group. The resulting unstable betaine either decomposes into the initial compounds or gives rise to an oxiran via nucleophilic substitution of the sulphide group by the anionic oxygen atom. The mode of decomposition is determined by the nature of the substituents in both the ylide and in the carbonyl compound. It is noteworthy that stabilised sulphonium ylides give rise to oxirans only by reacting with very reactive carbonyl compounds such as dicarbonyl compounds, α-halogenoaldehydes, etc.[109,189]:

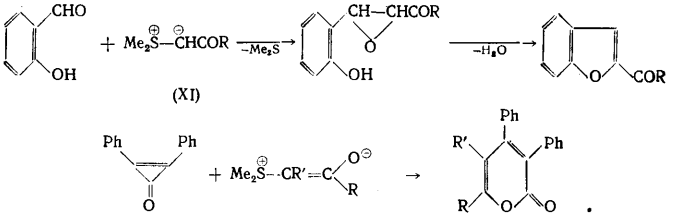


The introduction of a phosphoranylidene substituent in the α-position with respect to the carbonyl group of the sulphonium ylide increases the reactivity of the latter by reducing the involvement of the carbonyl group in the delocalisation of the negative charge over the sulphuranylidene fragment. This ylide reacts readily with carbonyl compounds, epoxidation predominating over "olefination":[190]



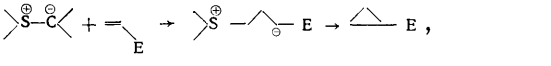
(50%) (25%)

The reactions of sulphonium ylides with aldehydes having a nucleophilic centre located close to the carbonyl group are of interest. Thus oxiran, formed when salicylaldehyde is used, is converted into benzofuran derivatives[191]. The reaction of sulphonium ylides with diphenylcyclopropenone, leading to 2-pyrones, is also unusual[192]:



(XI)

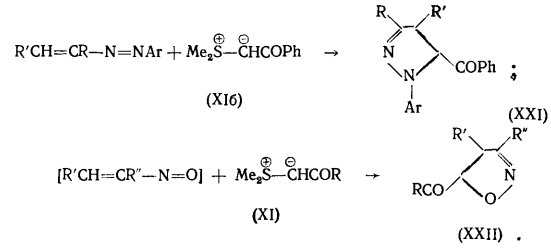
Stabilised sulphonium ylides react readily with olefins activated by electron-accepting substituents and in the case of α,β-unsaturated carbonyl compounds the conversion into a cyclopropane derivative predominates over epoxidation. Here one should note immediately that one is dealing only with the conversion of olefins into cyclopropane derivatives by fairly nucleophilic ylides stabilised by a single electron-accepting group, since in the presence of two such groups the ylide does not react with an extremely reactive chalcone[5]. The role of the electron-accepting substituent in the olefin consists not only in activating the double bond but also in stabilising the intermediate betaine. The specific synthesis of analogues of the latter confirmed the ready conversion of such betaines into cyclopropane derivatives[193]:



where E is an electron-accepting group.

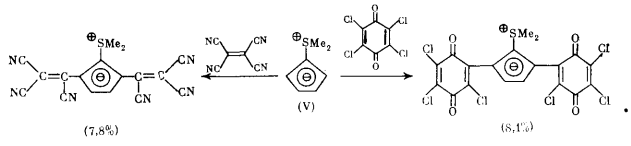
In recent years the reactions of stabilised sulphonium ylides with activated olefins have been used successfully to synthesise cyclopropyl-substituted heterocycles[194–196], sugars[197–200], phosphonium ylides[190], phosphonates[46], and phosphonium salts[201]. It is noteworthy that, when olefins with a conjugated system of multiple bonds are used in reactions of this kind, there is a possibility of the formation of not only the 1,2-addition products but also of 1,4-addition products, which can be due to the stereochemistry of this reaction[5,198–200]. The formation of 1,4-addition products has been recently demonstrated in the reactions of azoalkenes[202], nitrosoalkenes[203,204], and nitroalkenes[197–200] with sulphonium ylides, whereupon derivatives of 4,5-dihydropyrazoline

(XXI), Δ^2-isoxazoline (XXII), and Δ^2-isoxazoline *N*-oxide respectively were obtained:

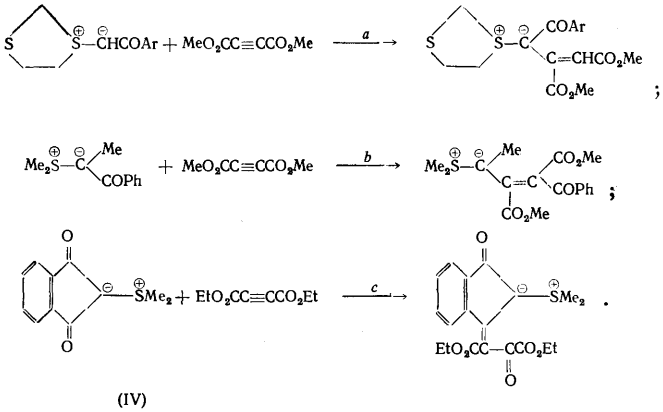


The reactions of sulphuranylidene derivatives of cyclopentadiene (V) with tetracyanoethylene and chloranyl entail the condensation of the latter two compounds at the β-carbon atom of the cyclopentadienyl ring, leading to products of the Michael addition (albeit in a low yield):[185]

Scheme 4



Stabilised sulphonium ylides react readily with alkynes, activated by electron-accepting groups, via pathways *a–c*, which depend on the structure of the ylide and the reaction conditions:



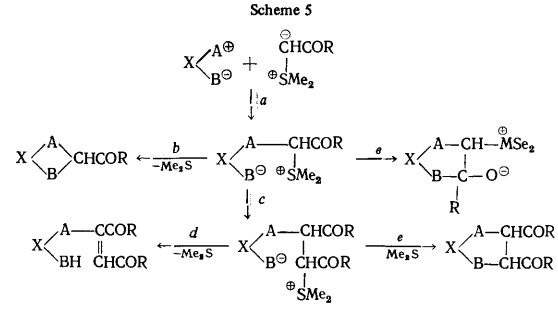
The use of protic solvents and ylides with a proton at the carbanionic carbon atom leads to the formation of new ylides via proton transfer (pathway *a*).[205] In aprotic solvents and for ylides with a disubstituted carbanionic carbon atom, new ylides are formed via the 1,3-migration of the acyl group (pathway *b*).[206] It is noteworthy that allyl-substituted ylides, formed via pathways *a* and *b*, can be cyclised into furan derivatives on heating or using DMSO as the solvent[206].

Pathway *c* obtains in reactions of sulphuranylidene derivatives of cyclic β-dicarbonyl compounds[207]. Here the alkyne adds to the carbonyl group of the enolate form of the ylide with formation and subsequent opening of the oxetan ring, which leads to products resulting from the transfer of the carbonyl oxygen.

One of the most important methods of synthesis of heterocycles is known to involve 1,3-dipolar cycloaddition reactions[208]. The reactions of 1,3-dipolar compounds with sulphonium ylides give rise to new possibilities in this sense.

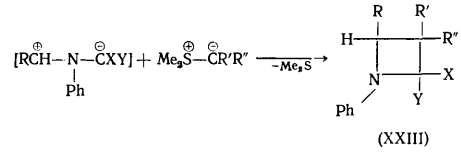
The study of the available literature data makes it possible to formulate six principal reactions of ylides with 1,3-dipolar compounds (*a–f*):

Scheme 5



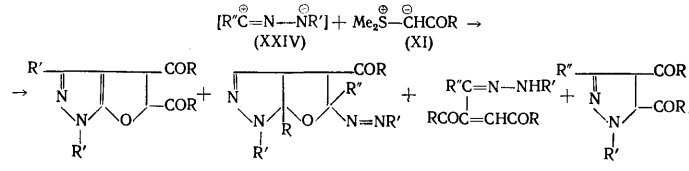
where $\overset{\oplus}{A}-X-\overset{\ominus}{B}$ are 1,3-dipolar compounds (for examples, see below).

In all cases the reaction begins with nucleophilic attack by the carbanionic carbon atom of the ylide on the electrophilic centre of the 1,3-dipole (*a*). The further course of the reaction depends on the nature of the 1,3-dipole and the substituents in the ylide. Thus azetidines (XXIII) are readily formed in the reactions of azomethine and sulphonium ylides (*b*):[209]



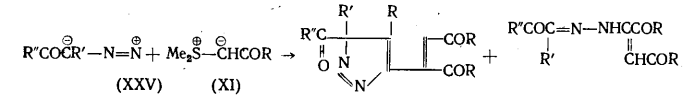
Pathway *b* is unfavourable when the 1,3-dipole contains two or three heteroatoms (nitrile imines, diazocarbonyl compounds, and azides), probably owing to the instability of the corresponding four-membered heterocycles. Depending on the structure of the ylide and the 1,3-dipole as well as the reaction conditions, products of pathways *c–f* are formed in this case.

The following products have been isolated in the reactions of sulphonium ylides with nitrile imines (XXIV):[204,210]



The formation of bicyclic adducts in this reaction shows that the growth of the "ylide chain" takes place not only in the betaines formed in reactions *a* and *d*, but also in the product of reaction *c*, both sulphonium and nitrile imine ylides being involved in its formation.

The reaction of ylides with diazocarbonyl compounds (XXV) is analogous albeit less varied (simple diazo-compounds do not undergo this reaction)[204,211]

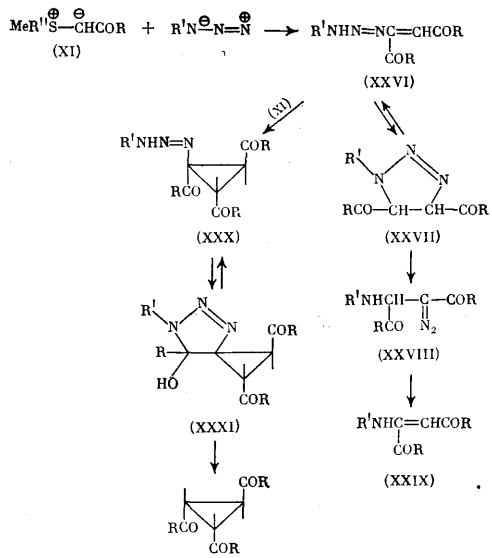


The difference between the structures of the products formed in the reactions of ylides with nitrile imines and diazocarbonyl compounds is evidently due both to the opposite polarisations of the corresponding 1,3-dipoles and to the

different relative reactivities of the 1,3-dipole compound and the intermediate betaines.

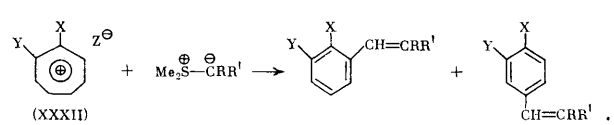
With the exception of alkyl azides[101,204], azides react with sulphonium ylides via pathways *d* and *f*.[101,102,204,212,213] The betaine (XXVI), formed via pathway *d*, can be stabilised by cyclisation to Δ^2-triazoline (XXVII), these forms being readily interconverted. In the presence of bases Δ^2-triazoline (XXVII) is unstable and decomposes to the diazo-compound (XXVIII) and then further (with loss of nitrogen) to the enamine (XXIX). Furthermore, the betaine (XXVI) can combine with a third ylide molecule to form cyclopropane derivatives of triazene (XXX) or Δ^2-triazoline (XXXI). The latter can decompose into the initial azide and a cyclopropane derivative:

Scheme 6



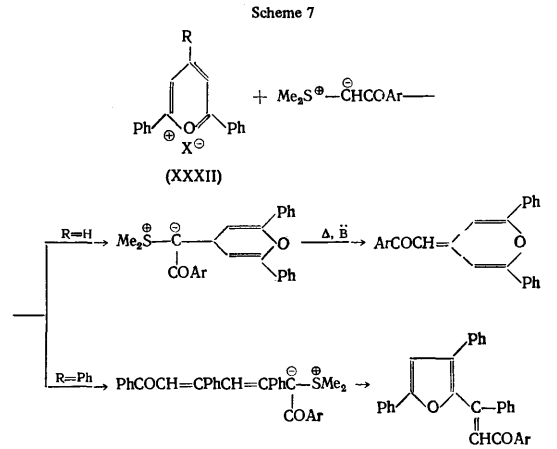
Studies devoted to the reaction of sulphonium ylides with tropylium[214–216], pyrylium[88,217,218], quinazolinium[219], oxathiolium, and dithiolium[220] have been published in recent years.

The reaction of sulphonium ylides with tropylium cations (XXXII) proceeds under mild conditions with formation of substituted styrenes[214–216]. The driving force of this reaction is provided by the formation of a stable benzene ring. By varying the substituents in the reactants, it has been shown that the mode of reaction is influenced by the steric hindrance arising during it and not by the nucleophilic properties of the ylide carbanion[214,215]. The attempts to isolate the intermediate sulphonium salts in these reactions proved unsuccessful, which can be accounted for by the ready elimination of the sulphide[216]:

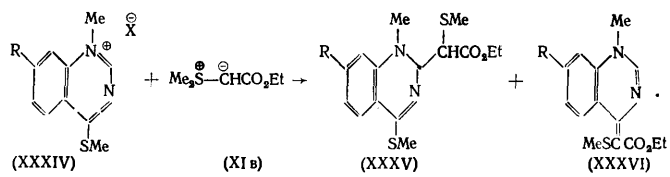


Pyrylium salts (XXXIII) are attacked by the ylide carbanion in the 2-position[88,217,218] or the 4-position[217] of the pyrylium heterocycle. The resulting sulphonium ylides decompose further to furan and 4-phenacylidenepyran derivatives respectively:

Scheme 7



In the reactions of sulphonium ylides with quinazolinium salts (XXXIV) the ylide attacks the 2- or 4-position in the heterocycle with formation of sulphonium salts. The latter are dealkylated by the nucleophilic counterion to give the products of $C_{(2)}$-substitution [compound (XXXV)] and $C_{(4)}$-substitution [compound (XXXVI)] in proportions which are determined by the nucleophilic properties of the anion[219], instead of the expected 1,4-benzodiazepines:

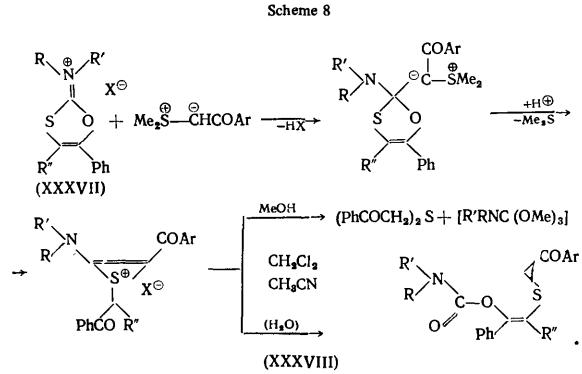


The yields of products (XXXV) and (XXXVI) are given below:

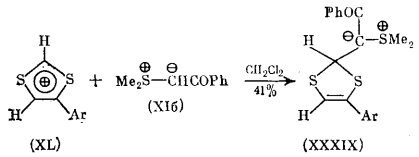
X	Yield of (XXXV), %	Yield of (XXXVI), %
OH	80	—
NO_3	0÷5	90

The oxathiolium cations (XXXVII) are highly reactive electrophiles. The structure of the products formed in their reactions with sulphonium ylides depends on the nature of the solvent employed. Carbamate esters (XXXVIII) are formed in aprotic solvents and diphenacyl sulphide is the product in protic solvents[220]. The overall mechanism of these reactions is presented in Scheme 8.

Scheme 8



The reaction proceeds via the nucleophilic attack by the ylide carbanion on the 2-position in the oxathiole ring. This has been confirmed by the isolation of the intermediate ylide (XXXIX) in the reaction of the dithiolium cation (XL) with the sulphonium ylide (XIb):



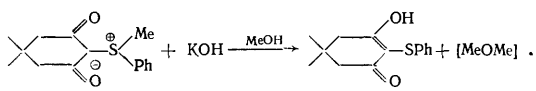
The rearrangement of the ylide, accompanied by the elimination of the sulphide, gives rise to the thi-irenium cation, whose hydrolysis and alcoholysis take place differently and lead to the observed products. The possibility of the existence of the thi-irenium cation has been recently confirmed by the synthesis and investigation of the stable 2,3-di-t-butyl-1-methylthi-irenium tetrafluoroborate[221].

Thus the reactions of stabilised sulphonium ylides with electrophiles constitute a convenient method of synthesising a wide variety of organic compounds, in the first place various carbocycles and heterocycles.

VI. REACTIONS WITH NUCLEOPHILES

The reactions of sulphonium ylides with nucleophiles lead in most instances to results similar to those described for their reactions with electrophiles. This is not surprising, since the reactions of ylides with water, alkoxides, and mercaptans proceed via the initial protonation of the ylide and subsequent attack by the nucleophile on the resulting sulphonium salt. The mode of decomposition of the latter depends both on the nature of the substituents at the sulphonium centre and on the nature of the nucleophile.

Thus the hydrolysis and alcholysis of ylides result mainly in the dealkylation of the sulphonium cation[222–226]:



If the ylide has been stabilised by ester groups, then the dealkylation is accompanied by hydrolysis and the elimination of ester groups[222]. The latter occurs sometimes even without the cleavage of the C–S ylide linkage, leading to the formation of a sulphobetaine[56,57,160,227,228].

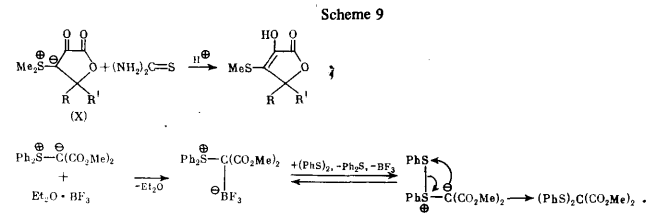
In constrast to what has been stated above, the reactions of sulphonium ylides with mercaptans lead mainly to the cleavage of the C–S ylide linkage[64,141,229,230]:

$$R_2\overset{\oplus}{S}-\overset{\ominus}{C}(COR')\,R'' + R'''SH \rightarrow R'''SCH(COR')\,R'' + R_2S\ .$$

The reactions of sulphonium ylides with cyanide[141] and phosphorodithioate[231] anions as well as the anions of compounds containing an active methylene group[232] take place similarly.

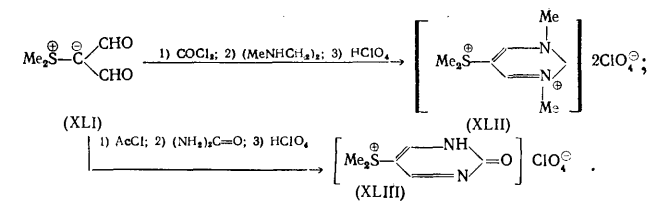
The reactions of thiourea[64] and disulphides[233] with sulphonium ylides take place only in the presence of a proton donor[64] or boron trifluoride etherate[233], i.e. they also involve the intermediate formation of sulphonium compounds:

Scheme 9



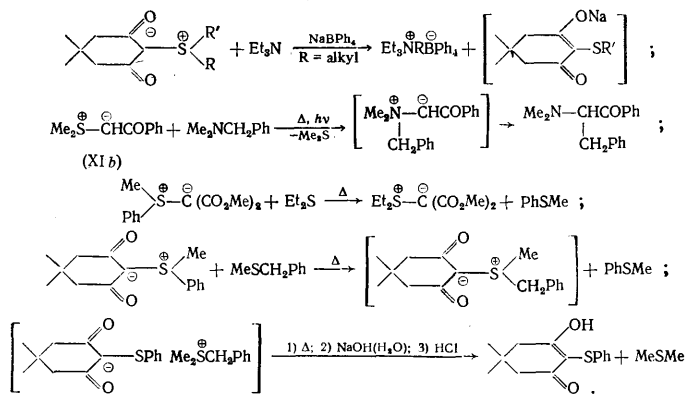
It is noteworthy that more nucleophilic monocarbonyl-stabilised ylides react with disulphides in the absence of a catalyst[233]. In this case the disulphide apparently reacts as an electrophile in a manner similar to that described in Section V.

The reactions of dimethylsulphuranylidenemalonic aldehyde (XLI) with urea and *N,N'*-dimethylethylenediamine are of interest; under these conditions, the condensation reactions lead to the formation of heterocyclic sulphonium salts (XLII) and (XLIII).[85] The authors noted that phosgene and acetyl chloride are used in these reactions to convert the ylide into a more reactive form:



Stabilised sulphonium ylides react in two ways with tertiary amines[57,234] and dialkyl sulphides[139,235], giving rise to transylidation products[57,139] or the product of the dealkylation of the ylides[234,235]:

Scheme 10

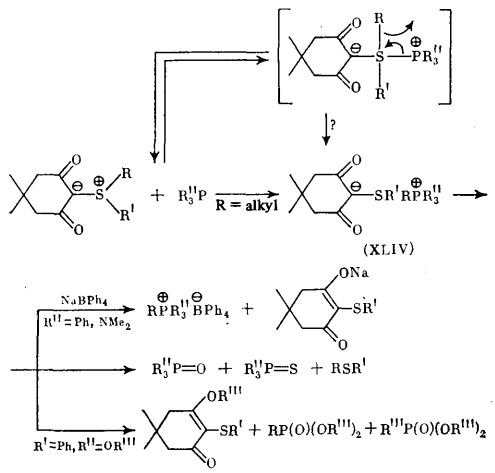


The transylidation reactions of sulphonium ylides with amines and sulphides can be greatly facilitated by carrying them out in the presence of catalytic amounts of dialkoxydisulphides, thiocyanogen, aryl thiocyanates, *p*-hydroxyphenyl trifluoromethyl sulphide, etc.[69,139,144,236]

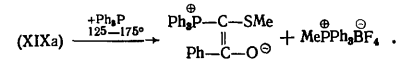
Stabilised sulphonium ylides react with Ph_3P,[162,237–243] $(Me_2N)_3P$,[242–244] and $P(OR)_3$.[243,245] The structures of the products formed in these reactions depend both on the

nature of the substituents in the ylide and on the nature of the substituents in the phosphorus(III) derivative. In the reactions of sulphuranylidene derivatives of dimedone and benzenesulphonylacetophenone with phosphorus(III) derivatives the ylide is dealkylated, which leads to phosphonium salts with an enolate anion[240–245]. Alkyltriphenylphosphonium salts, obtained in the reactions of *S,S*-alkylphenylsulphuranylidine derivatives of dimedone (XLIV) and benzenesulphonylacetophenone were isolated from the reaction products. In the remaining cases they decomposed in the course of the reaction with formation of the products presented in Scheme 11:[214,243,246]:

Scheme 11

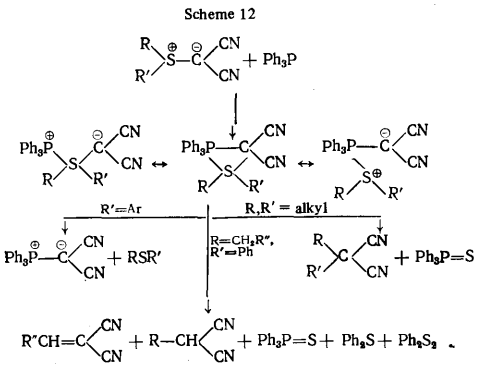


The reaction of the phenacylide salt (XIXa) with Ph_3P proceeds similarly[162]:



The replacement of the carbonyl and sulphonyl groups in the ylide by nitrile groups in the reactions of sulphuranylidene derivatives of dicyanomethane with Ph_3P leads to transylidation or ylide transalkylation–desulphurisation products[237–239]. The mode of reaction is determined by the nature of the substituents at the sulphonium sulphur atom:

Scheme 12



The phosphonium salts formed in the dealkylation of ylides can be obtained either by the intermediate formation and decomposition of σ-sulphuranes or by the direct attack of the phosphorus nucleophile on the electrophilic carbon atom of the *S*-alkyl group. The latter pathway appears to us to be preferable.

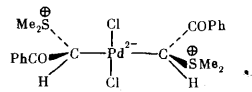
The formation of all the products detected in the reactions of sulphonium ylides with phosphorus(III) derivatives can be accounted for by the intermediated formation and decomposition of phosphonium salts[243,246]. The reactions of diarylsulphuranylidenedicyanomethanes with Ph_3P, where the attack of the latter on the sp^2-hybridised carbon atom of the *S*-aryl group is hindered, constitute an exception[247]. In such cases the mechanism involving the insertion of Ph_3P in the C–S ylide linkage apparently takes place with formation of a resonance-stabilised triad, whose decomposition leads to the observed products[237–239].

It is noteworthy that carbonyl-stabilised sulphonium ylides are dealkylated not only by phosphorus(III) and nitrogen derivatives[234,240–245] but also by tertiary arsines[248], triphenylstibine, and triphenylbismuth[234].

VII. ORGANOMETALLIC DERIVATIVES AND COMPLEXES

It was stated in Section V that stabilised sulphonium ylides react only with olefins activated by electron-accepting substituents. However, it is known that the electrophilic properties of an olefin are enhanced when it forms complexes with transition metal (platinum and palladium) salts[249]. This stimulated attempts to convert olefinic ligands into cyclopropane derivatives in transition metal complexes. However, it was found that, instead of the formation of a cyclopropane derivative, the olefin is readily substituted by the ylide under these conditions[250,251]. Such complexes can be obtained not only by ligand exchange[250–255] but also by their direct synthesis from ylides and metal salts[19,256,257], the structure of the complex formed depending on the nature of the metal, the structure of the ylide, and, in the case of exchange reactions, the structure of the initial complex. Thus sulphuranylidene derivatives of acetophenone form 2 : 1 adducts with $PdCl_2$ or $PdBr_2$,[68,250–252,256,257], 2 : 1 or 1 : 1 adducts with PtCl, depending on the method of synthesis[253,256], and dimers of 1 : 1 adducts with $HgCl_2$, evidently incorporating bridging chlorine atoms[256]. The formation of 1 : 1 adducts is also observed in the formation of complexes of sulphuranylidene derivatives of cyclopentadiene with HgI_2, $ZnCl_2$, and $AgNO_3$,[19] and of the dimethylsulphuranylidene derivative of malonic aldehyde (XLIII) with ZnI_2.[85]

The study of the ^1H and ^{13}C NMR and infrared spectra of the complexes of sulphuranylidene derivatives of acetophenone showed that the metal is coordinated to the carbanionic carbon atom of the ylide[68,250–253,256]. According to the results of X-ray diffraction analysis, the 2 : 1 complexes with $PdCl_2$ have the square planar *d,l-trans*-configuration[250,251]; when they are dissolved, epimerisation takes place readily and the ^1H NMR spectra demonstrate the existence of a mixture of *meso*- and *d,l-trans*-forms:[251]



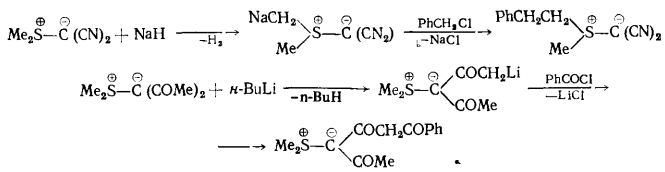
The structure of the complexes of PtX_2 with ylide ligands is influenced by the nature of the halogen[252,253], the amount of the *trans*-isomer increasing under these conditions in the sequence X = Cl < Br < I, which is analogous to that observed for the complexes $PtX_2.(Et_3P)_2$.[258]

The metal atom can be coordinated not only to the carbanionic carbon atom of the ylide but also to a sulphur atom[19,259] or a nitrogen atom, for example in complexes of dimethylsulphuranylidenedicyanomethane (III) with $PdCl_2$.[259] The absence of the coordination of the metal to the carbon atom in the latter case is probably caused by its reduced nucleophilicity due to the delocalisation of the electron density

over the electron-accepting cyano-groups. In the sulphuranylidene derivatives of cyclopentadiene (V) the metal can be coordinated not only to the sulphur atom[19] but, as shown recently in relation to their complexes with chromium, molybdenum, and tungsten carbonyls[260], also to the cyclopentadienyl system.

It was noted in Section VI that the coordination of Lewis acids to the carbanionic carbon atom of the ylide facilitates their reaction with nucleophiles. In this connection attempts were made to investigate the reactions of nucleophiles with ylides functioning as ligands in transition metal complexes. However, it was found that this entails only ligand exchange reactions. Thus it has been found[251] that pyridine substitutes one ylide ligand in the cold and both ylide ligands on heating 2 : 1 complexes of sulphuranylidene derivatives of acetophenone with $PdCl_2$.

Organometallic derivatives of stabilised sulphonium ylides are readily formed on metallation of ylides with BuLi, iso-Pr_2NLi,[261,262] or NaH,[142] a proton being substituted both in the substituent at the carbanionic carbon atom[261,262] and at the *S*-alkyl group[142]. Their further reactions are of the usual type for organometallic compounds:



VIII. PRACTICAL APPLICATIONS

Intensive investigation of the chemistry of sulphonium ylides began approximately 15 years ago and during this relatively short period interesting practical results have been obtained. Sulphonium ylides proved to be effective nucleophiles for the epoxidation of carbonyl compounds and the conversion of olefins into cyclopropane derivatives[5,263]. This constitutes an important addition to the methods for the epoxidation and conversion into cyclopropane derivatives by electrophilic carbenes[264]. The use of ylides for the synthesis of heterocycles is also extremely important[265]. This review presents the results of synthetic applications of stabilised sulphonium ylides. However, this does not exhaust their applications. It has been suggested that sulphonium ylides be used as catalysts of the liquid-phase oxidation of hydrocarbons[266]. There are data showing that 4-dialkylsulphuranylidene-2,6-di-t-butylcyclohexadienones[267] effectively alkylate compounds containing an acidic proton[268]. Diphenylsulphuranylideneacetone and its analogues make it possible to obtain products used to prepare modifying agents for paper, textiles, and leather as well as substances used in the manufacture of polyamides, polyesters, alkyd resins, and plant protecting agents[269].

Sulphuranylidene derivatives of cyclopentadiene accelerate the dyeing of polyester, polyamide, and other fibres by anionic dyes[270]. Dimethylsulphuranylidene-*p*-nitrophenacyloxyethoxycarbonylmethane exhibits a fungicidal activity[271], while 3-dialkylsulphuranylidene-2-oxo-1,4-naphthoquinones exhibit an anti-inflammatory inactivity and can be used in the treatment of arthritis, erythema, oedema, etc.[272]

Thus the range of applications of sulphonium ylides is wide and varied extending from reagents for organic syntheses to effective physiologically active preparations. New studies in this field will undoubtedly lead to a wider practical utilisation of these substances.

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Chromatography in the Gas-Liquid Crystal System

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The analytical and physicochemical aspects of chromatography using liquid-crystal sorbents are examined and it is concluded that liquid crystals exhibit a unique separating capacity in the analysis of structural isomers. The possibility of using liquid crystals as universal sorbents with a controllable selectivity and suitable for the solution of various analytical problems is demonstrated. The results of the study of the thermodynamics of the sorption of substances by liquid crystals, phase transitions and preceding effects, etc. are presented.
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I. INTRODUCTION

Liquid crystal compounds have been known for about 100 years, but their application in gas chromatography began comparatively recently[1]. The interest in liquid crystals for chromatography is due to the possibility of using them as selective sorbents for the separation of structural isomers, particularly *p*- and *m*-substituted benzenes, whose separation is difficult on the usual isotropic liquids. Reviews have been devoted to the use of liquid crystals in chromatography[2-7]. There is no doubt that *meta*–paraselectivity should be regarded as the principal parameter of the operation of such stationary phases. However, at the present stage of the investigation of the liquid-crystal sorbents it is no longer possible to restrict the treatment to this characteristic. This review deals with problems concerning a more far-reaching study of the sorption properties of mesomorphic compounds in all regions of their phase state, the determination of the position of liquid crystals among other stationary phases, the discovery of the analytical possibilities of liquid-crystal sorbents, the study of phase transitions of the thermodynamics of the dissolution of substances in the isotropic and anisotropic regions, and of the thermal stability of liquid crystals, the investigation of their viscous properties and the associated efficiency of chromatographic columns, the study of mixed phases based on liquid crystals, etc.

The term "liquid crystal" was first introduced by Lehmann[8] for compounds which are characterised, within a certain temperature range, simultaneously by the properties of both liquids (high fluidity, the ability to form drops, etc.) and crystals (optical, magnetic, and electrical anisotropy).

A liquid does not have the three-dimensional order characteristic of a crystal. However, the idea of a liquid as a completely amorphous phase in which the molecules are distributed at random, like the molecules of a gas, is not correct. Studies on the scattering of light and X-rays[9] have shown that there is a short-range order in the arrangement of the molecules in a liquid, i.e. they possess the elements of a crystal structure. The similarity between the liquid and solid states increases when the molecules of the given substance have a planar and extended shape. This favours a more compact packing of the latter and, in the presence of sufficient attraction forces, can lead to the formation of large numbers of molecules oriented in parallel planes. Mesomorphism is observed most often among aromatic compounds. Liquid-crystal compounds containing benzene and naphthalene rings are known. An important group of liquid crystals can be made up of derivatives of cholesterol or compounds with a cyclopentanoperhydrophenanthrene group.

Thus the liquid-crystal state, characteristic of compounds whose molecules have an elongated linear shape with polarisable groups in the structural skeleton, is distinguished by a specific orientation of these molecules in space, involving the arrangement of their longitudinal axes parallel to one another. Liquid crystals are most often formed by compounds whose molecules consist of extended chains incorporating planar aromatic rings with substituents in the *para*-position in the benzene ring; in the presence of substituents in the *ortho*- or *meta*-position, the capacity for the formation of the liquid crystal disappears. An example of a liquid-crystal compound with a single benzene ring is provided by *trans*-*p*-methoxycinnamic acid. The tendency towards mesomorphism increases with increase of the number of connected benzene rings. Groups connecting benzene rings into a chain play a major role. Compounds forming liquid crystals have been described in a series of reviews and monographs[2,3,10-14] and the physical properties and classification of liquid crystals have also been described[2,10,11]. Liquid crystals are much more rarely formed by aliphatic compounds. The explanation is probably the relative flexibility of the long chains in compounds of the paraffinic series.

Liquid crystals can be divided into two main groups. Those in one group are classified as thermotropic liquid crystals; compounds in this class are obtained by heating a solid and exist only in a specific temperature range. Lyotropic liquid crystals constitute the second group and are obtained by mixing two or several components, an amphiphile being usually one of the components. Since only thermotropic liquid crystals are at present used in chromatography, we confine ourselves to the consideration of this class of mesomorphic substances, which include two main types: smectic and nematic; the cholesteric phase is assumed to be a variety of the nematic phase.

When many substances melt, a smectic phase is formed initially in which the molecules are not only arranged parallel to one another but also are fixed in layers; at higher temperatures there is a transition to the nematic phase where this additional order disappears. Cholesteric liquid

crystals are characterised by a helical molecular structure. A single substance has been found containing both nematic and cholesteric phases although individual substances can exist as smectic-nematic or smectic-cholesteric mesophases. The mesophase exists within a specific temperature range characteristic of each substance. When the temperature changes outside the limits of this range, either the usual solid crystal (decrease of temperature) or the isotropic liquid (increase of temperature) is formed.

The most important characteristics of liquid crystals are the melting point involving the transition from the solid state to the mesophase, the point of transition from one mesophase to another, and the clarification point (transition from the liquid-crystal state to the isotropic liquid). Studies have not as yet led to the discovery of a rigorous relation between the structure of the liquid-crystal substance and the type of mesophase, on the one hand, and the selectivity with respect to the *meta*- and *para*-isomers, on the other. Intense investigation of this problem by comparing the experimental results for the variation of molecular structures as well as studies of the influence of a substituent in homologous series led to the discovery of a series of necessary conditions ensuring the maximum steric effect of the mesophase.

II. ANALYSIS OF STRUCTURAL ISOMERS

The first studies of the chromatographic characteristics of liquid crystals already demonstrated their probable usefulness as sorbents for gas chromatography[1,15]. The interaction forces in a sorbate–liquid-crystal melt system, due to the ordered arrangement of molecules in the temperature range of the mesophase, promote the separation of aromatic *meta*- and *para*-isomers with similar boiling points. This effect, first observed by Kelker[1,15] and Dewar and Schroder[16] using *p,p'*-azoxyanisole, proved to be characteristic of many liquid crystals; it is associated with the fact that the more closely linear form of the molecule of the *para*-isomer compared with the *meta*-isomer enables the former to penetrate more readily into the lattice of the liquid crystal and is accordingly more strongly retained by the latter in the temperature range of the mesophase. Above the clarification point, the order of elution of isomers is usually determined by their boiling points[5].

The results of the above investigations led to extensive analytical use of liquid-crystal sorbents[15–71]. The following mixtures have been analysed on columns of liquid crystals: isomeric xylenes[1–6,15–19,22–28,31–44], butylbenzenes[45], vinyltoluenes[46,47], divinylbenzenes[48], mono- and dimethylnaphthalenes[26,46,49], various derivatives of benzene[22,39,41,42], naphthalenes[50–54], and phenol[55], isomers of benefin [*N*-(n-butyl)-*N*-ethyl-2,6-dinitro-α,α,α,-trifluoro-*p*-toluidine] and trifluralin (2,6-dinitro-*N*,*N*-di-n-propyl-α,α,α-trifluoro-*p*-toluidine)[56], isomers of benoxaprofen [2-(4-chlorophenyl)-α-methylbenzoxazole-5-acetic acid][57], terpenes and their derivatives[58], enantiomers of *N*-perfluoroacyl-2-aminoethylbenzene[59,61], steroids[62], heterocyclic aza-compounds[63], polyaromatic hydrocarbons[53,64–66,69–70], cholic acids and α,β-steroid epimers[64,67,68], and pheromone isomers[71]. At the same time extensive studies have been made on the sorption characteristics of liquid crystals and the thermodynamics of the sorption of different substances by the latter. Studies on these lines have been carried out by Kelker and coworkers[2,17,20,21], Dewar and Schroeder[22,23], Barrall et al.[24], Vigdergauz and coworkers[25–28], Chow and Martire[29,30], etc. Studies have been made on the sorption properties of *p,p'*-azoxyphenetole, a homologue of *p,p'*-azoxyanisole, with a nematic phase existing in the range 138–168 °C, in relation to a large number of paraffinic, naphthenic, and aromatic hydrocarbons[2,15].

A remarkable property of the nematic mesophase of *p,p'*-azoxyphenetole is its high selectivity with respect to positional isomers. Thus the ratio of the retention volumes of *p*- and *m*-xylenes on the above sorbent in the region of the mesophase at 140 °C is $\sigma_H = 1.09–1.10$. Comparison of this quantity with the values obtained[72] for phenanthrene and 7,8-benzoquinoline, used previously for the separation of xylene isomers, indicates a greater selectivity of *p,p'*-azoxyphenetole. Among other aromatic compounds used for the separation of isomeric xylenes, one may mention halogenophthalates, α-naphthylamine ($\sigma_H = 1.089$), 1,8-diaminonaphthalene ($\sigma_H = 1.09$), m-phenylenediamine ($\sigma_H = 1.05$), α,α'-bipyridyl ($\sigma_H = 1.06$), and *p*-aminoazobenzene ($\sigma_H = 1.05$).[73] These substances proved to be less selective stationary phases than *p,p'*-azoxyphenetole.

The ratios of the retention volumes of the isomeric xylenes (σ_H) on Bentone-34 modified with a silicone oil (in 1:1 proportions) and dinonyl phthalate (60:40) are 1.13 and 1.14 respectively[73]. However, one should point out that Bentone-34 is a technical product consisting of bentonite clay treated with an ammonium base; in particular, Bentone-34 is dimethyloctadecylammonium bentonite. The characteristics of the clay vary from batch to batch, giving rise to difficulties in the exchange reaction with the ammonia base, whence follows the poor reproducibility of the retention characteristics. The non-uniformity of the distribution of isomeric xylenes requires the modification of bentone with a silicone or dinonyl phthalate in appropriate proportions. As a consequence of the non-reproducibility of the results, this ratio also varies from batch to batch. Compared with bentones, liquid crystals have the following advantage: being individual organic compounds and being fairly pure, they ensure the reproducibility of the selective properties and a uniform distribution of isomeric xylenes on the chromatogram[73–76].

The analytical possibilities of *p,p'*-azoxyphenetole have been illustrated in relation to the separation of bicyclic hydrocarbons—mono- and di-methylnaphthalene. The employment of the usual stationary phases, such as cable oil, Apiezon, poly(ethylene glycol)-2000,[77,78] etc. precludes the complete separation of dimethylnaphthalenes as a consequence of the equality of the retention times of 2,6- and 2,7-, 1,3- and 1,6-, and 1,4-, 1,5-, and 2,3-dimethylnaphthalenes. On the other hand, these groups of isomers can be readily separated in the liquid-crystal region of *p,p'*-azoxyphenetole[26]. The retention volumes of alkylnaphthalenes measured in the range 110 to 150 °C indicate their different sorbabilities when the stationary phase passes from the solid to the liquid-crystal state and then to the isotropic liquid state. The elution sequence of alkylnaphthalenes for the solid and isotropic liquid states of the stationary phase is determined by their boiling points and the same dimethylnaphthalene isomers are non-separable as on columns with the usual stationary phases.

The situation is different for the liquid-crystal state of *p,p'*-azoxyphenetole. Here there is a distinct steric effect, which is seen already in relation to monomethylnaphthalenes where the α-isomer is eluted before the β-isomer at 137 °C, although it has a higher boiling point, i.e. the elution sequence is determined by the steric structure of the sorbates. The elution sequence is inverted also in the case of dimethylnaphthalenes. However, one should note that the comparatively low temperature of the analysis, corresponding to the maximum structural selectivity of

azoxyphenetole (137 °C), required a prolonged duration of analysis in the separation of such high-boiling compounds (2.5–3 h). The bisphenetidylterephthalaldehyde liquid crystal used for this purpose is characterised not only by a shorter separation time at 205 °C (down to 15–20 min) but also by a higher selectivity in relation to the isomers indicated[46].

Alkylnaphthalenes were later separated[49] in the nematic and supercooled region of *N,N'*-bis(*p*-methoxybezylidene)-α,α'-bis-*p*-toluidine with a temperature range of the nematic mesophase of 181–320 °C. This liquid crystal is extremely effective also in the separation of benephine from trifluralin[56], the benoxaprofen isomers[57], heterocyclic azacompounds[63], steroids[64,67,68], and polycyclic aromatic compounds[64–66,69–70]. Other examples of the use of the supercooled region of mesophases for the separation of isomers are available in the literature[18,22,24,33,79]. Among the liquid crystals synthesised, mention should be made of the asymmetric azoxyether *p,p'*-ethoxymethoxyazoxybenzene and *p*-methoxybenzylidene-*p'*-butyrylaniline[33,46].

It has been shown[33] that, for a temperature of the analysis close to the melting point of *p,p'*-ethoxymethoxyazoxybenzene, the ratio of the characteristics for *p*- and *m*-xylenes reaches 1.125–1.13, which leads to a significant improvement in the chromatographic separation of the isomers and to a uniform distribution of the peaks of aromatic hydrocarbons on the chromatogram. Isomeric vinyltoluenes have been separated on ethoxymethoxyazoxybenzene[46]. The use of columns with *p*-methoxybenzylidene-*p'*-butyrylaniline permitted the complete separation of aromatic C_8 isomers and isopropylbenzene[46]. It is noteworthy that isopropylbenzene is usually eluted together with *p*-xylene on the liquid-crystal azoxyethers investigated previously.

The elucidation of the influence of the width of the temperature range of the mesophase on the selectivity with respect to positional isomers and of the influence of the nature of the mesophase on the solvent power of the sorbent revealed a relation between these quantities and the *meta–para* selectivity, demonstrating the advantages of compounds with broad regions of the liquid-crystal state. This follows from the data of Kelker et al.[19] (Table 1).

Table 1.

Compound	t_{clar}, °C	t_m, °C	σ_H
4-Methoxybenzylidene-4'-cyanoaniline	117	106	1.03
p,p'-Azoxyanisole (I)	134.5	117	1.04
4-Methoxybenzylidene-4-acetoxyaniline	107	83	1.05
p,p'-Azoxyphenetole (II)	168	13	1.09
60% (I) + 40% (II) eutectic	146	97	1.10

Notation: t_{clar} = clarification temperature, t_m = melting point, and σ_H = selectivity coefficient defined at the ratio of the reduced retention times of the *m*- and *p*-complexes.

The temperature range of the mesophase can be expanded either by synthesising the appropriate liquid-crystal compound or by employing mixed phases forming a eutectic. In the latter case there is a corresponding decrease of the phase transition temperatures together with the expansion of the mesophase region. However, the results of subsequent studies[79,80] showed that the conclusion that the selectivity in relation to isomers varies in parallel with the width of the temperature range of the mesophase is valid only for liquid crystals with similar structures. This is evidently associated with the additional influence of the chemical nature of the sorbent on the selectivity.

This is why the compounds investigated by Kelker[53,81,82], Dewar and Schroeder[16,22], and Vigdergauz and coworkers[80,83] with the width of the temperature range of the nematic mesophase corresponding to 100 and more degrees, exhibit a much lower selectivity in relation to the positional isomers of xylene than *p,p'*-azoxyphenetole. The wide temperature range of the mesophase does not therefore alone guarantee a high selectivity of the sorbent in relation to positional isomers. Nevertheless the synthesis and use of such phases are promising from the analytical standpoint. The retention characteristics of substances on columns with sorbents at high temperatures (above 200 °C) and with broad temperature ranges of the nematic melt have been published[2]. In particular, one can recommend bisphenetidinylterephthalaldehyde (nematic region in the range 198–323 °C), which can be used successfully for the separation of high-boiling components: α- and β-naphthols, α- and γ-benzopyridines, dimethylphthalate, and dimethyl ethers derived from phenanthrene, anthracene, and carbazole, as well as "difficult" pairs of dimethylnaphthalenes[2,19,37,46]. Interesting results have also been obtained on 4,4-bis(benzylidene)benzidine and bis(*p*-methoxybenzylidene)-*trans*-4,4'-diaminostilbene[19].

Liquid-crystal compounds with a nematic mesophase have been most thoroughly investigated. There exist only a few examples of the use of liquid crystals of the smectic and cholesteric type. According to the theory of the liquid-crystal state, the smectic mesophase is characterised by a higher degree of order among the molecules; it therefore appears quite evident that it should exhibit a higher selectivity with respect to positional isomers compared with a nematic melt. However, the opposite behaviour has been most frequently observed in practice and unfortunately the higher order has not been fully realised. The explanation is that the majority of substances are highly viscous in the smectic state, the viscosities sometimes reaching values which cannot be measured on the usual viscometers and the phase transition from the smectic mesophase to the nematic mesophase is measured as the melting point. In this case the smectic region can be observed only by special methods (thermo-optics, thermography, etc.).[84,85]

Naturally the high viscosity of the smectic phase greatly hinders the diffusion of the components analysed for the latter, as a result of which the contribution of adsorption becomes decisive. Two competing factors act in the smectic region: the high degree of order of the molecules leads to the intensification of the *meta–para* selectivity, while viscosity has the opposite effect. Nevertheless one should point out the use of liquid crystal sorbents of the smectic type: ethyl *p,p'*-azoxybenzoate, ethyl *p*-ethoxybenzylideneaminocinnamate, and 4,4'-di-n-hexyloxy- or 4,4'-di-n-heptyloxy-azoxybenzene[15,16,22]. Unusual results have been obtained for a smectic ester, *p*-phenylene bis-*p'*-heptyloxybenzoate, which has a broad region corresponding to the existence of the smectic (79–125 °C) and nematic (125–199 °C) phases[22]. It has been shown that at 68 °C (the solid crystal region) the ratio of the retention parameters of *p*- and *m*-xylenes is 1.10, i.e. corresponds to the experimental structural selectivities of *p,p'*-azoxyphenetole in the eutectic mixture.

Dewar and Schroeder[22,23] noted short retention times of the sorbates and asymmetry of the peaks (the presence of tails) at 68 °C. The elution sequence is *m*- → *o*- → *p*-isomers. The chromatographic characteristics of *p*-phenylene bis-*p'*-heptyloxybenzoate were also examined in other studies[80,83]

in relation to a wide set of paraffinic, naphthenic, and aromatic hydrocarbons in the range 30–220 °C and it was shown that the *meta–para* selectivity of the ester began to be manifested only at 80 °C; this is apparently associated with a decrease of viscosity of sufficient for the contribution of adsorption forces to the retention of sorbates to become significant. The ratio of the retention parameters of *p*- and *m*-xylenes in the smectic region did not exceed 1.03, while in the region of the nematic phase (at 130 °C) it was 1.05.[83]

In the separation of hydrocarbons on *p*-(n-heptyloxy)-benzoic acid[83] an increased solubility of *p*-xylene in both the smectic (92–99 °C) and nematic (99–146.5 °C) mesophases was noted. At 94 °C the ratio of the retention parameters is 1.05 and remains the same at 100 °C (nematic region), i.e. the structural selectivities of both varieties of the mesophase are the same. The much lower selectivity of the acid with respect to the isomers compared with the eutectic mixture of *p,p'*-azoxyanisole and *p,p'*-azoxyphenetole shows that the equality of not only the temperature ranges but also of the absolute melting points and clarification temperatures does not guarantee identical structural selectivities of the sorbents.

An example of the practical utilisation of smectic liquid crystals is provided by the separation of optical isomers carried out by Lochmüller and coworkers[59–61] using optically active mesophases, namely the isopropyl ester of carbonylbis-D-leucine or the alkyl esters of L-valine. However, they showed that the efficiency of separation is in this case determined by chemical reactions, by the intermediate formation of diastereoisomers—hydrogen-bonded association complexes between the stationary phase and the pair of enantiomers. It is known that, apart from liquid crystals, another class of optically active compounds, namely dipeptides, have been used[86,87] for the separation of enantiomers.

The solvent power of cholesteric liquid crystals has been investigated by a number of workers[2,22,24,29,58] as well as Vigdergauz and coworkers[51,88]. A unique property of this mesophase is its high optical activity. In many instances the specific rotation of the plane of polarisation of light is 60000–70000 deg mm^{-1}, while in the case of the usual organic liquids it rarely exceeds 300 deg mm^{-1}. Such a high optical activity is due to the twist in the structure of cholesteric liquid crystals, i.e. a consistent "rotation" of the molecules in their mutual arrangement. It has been suggested that this structure of the mesophase permits the resolution of a racemic mixture into optically active isomers. However, such resolution could not be achieved[2]. Cholesteric liquid crystals did not exhibit an appreciable selectivity with respect to positional isomers either. Nevertheless, one should note that Porcaro and Schubiak[58] used successfully cholesteryl cinnamate together with other smectic and nematic mesophases for the separation of terpene derivatives.

When cholesteryl acetate was used as the stationary phase, the optical isomers of (±)-γ-lactones were separated[89]. The results of studies of the chromatographic characteristics of cholesteryl benzoate (the region of the mesophase is in the range 149–179.5 °C), cholesteryl acetate (94.5–116.5 °C), cholesteryl valerate (93–101.5 °C), and cholesteryl nonanoate (smectic region in the range 77.5–80.5 °C and cholesteric region in the range 80.5–92 °C) in relation to the separation of C_7–C_{10} paraffinic hydrocarbons and aromatic hydrocarbons (benzene, toluene, and ethylbenzene) have also been published[17,24]. The esters investigated exhibited the same features on dissolution of the sorbates as other types of liquid-crystal mesophases, altering the retention characteristics in the case of phase transitions.

The data of Barrall et al.[24], who established a relation between the group selectivity of cholesterol esters in the region of the mesophase and the length of the paraffin chain of the esters, are of interest. Thus, in their isotropic state (120 °C) these cholesterol ester sorbents gave rise to virtually identical retention characteristics of the paraffinic and aromatic hydrocarbons, while in the region of the mesophase the retention of paraffins by cholesteryl nonanoate was much stronger than by other esters. This is apparently a consequence of the interaction of paraffins with long-chain esters, since the retention of aromatic-hydrocarbons is in this case weaker than that of aliphatic hydrocarbons with the same number of carbon atoms in the molecules.

Extensive analytical possibilities arise when mixed sorbents based on liquid crystals are used. Thus, a detailed study has been made[18] of the chromatographic and thermo-optical behaviour of a mixture of cholesteryl benzoate and *p,p'*-azoxyphenetole in relation to the separation of isomeric xylenes. A detailed investigation has been made[88] of the properties of binary sorbents, in the first place those in which one of the ingredients is a liquid-crystal compound [for example, in the separation of dimethylnaphthalenes on compound columns containing *p,p'*-azoxyphenetole and poly(ethylene glycol)-2000; the ratio of the amounts of the stationary phases then corresponds to the ratio of the lengths of the compound column sections indicated] and, in the second place, those in which both ingredients are in the liquid-crystal state. Thus, the authors[88] examined binary mixtures incorporating *p,p'*-azoxyphenetole, *p*-(n-heptyloxy)benzoic acid, the ester of hydroquinone and *p*-(n-heptyloxy)benzoic acid, and cholesteryl cinnamate; the sorbates employed were C_9–C_{11} n-paraffins and *m*- and *p*-xylenes. Deviations were observed from additivity in the retention of sorbates as a function of the composition of the mixed stationary phase. The corresponding deviations are determined both by the energy of the interaction of the components of the stationary phase and by the additional energy of the interaction of the sorbate with the mixture formed.

Eutectic mixtures of nematic mesophases are of greatest interest for chromatography. Studies in this field have been carried out by Kelker[2,19] and the authors of the present review[26,35]. Thus the eutectic mixture *p,p'*-azoxyanisole and *p,p'*-azoxyphenetole in molar proportions of 60:40 was characterised by a high selectivity in the separation of *p*- and *m*-xylenes (the ratio of the reduced retention times was $\sigma_H = 1.11$). Similarly Vigdergauz et al.[26] investigated mixtures of liquid crystals in molar proportions of 20:80, 55:45, 60:35, and 80:20. Andrews et al.[38] studied binary mixtures made up to *p,p'*-dimethoxyazoxybenzene (azoxy-anisole), *p,p'*-diethoxyazoxybenzene (azoxyphenetole), *p,p'*-dibutoxyazoxybenzene, and *p,p'*-dihexyloxyazoxybenzene. The composition of the eutectics of the above liquid crystals was found by recording the phase diagrams. All the eutectics without exception exhibited a much greater structural selectivity than their components. The greatest selectivity was shown by the mixture of *p,p'*-azoxyphenetole and *p,p'*-dibutoxyazoxybenzene (molar ratio 38:62, $\sigma_H = 1.13$). Deviations were then found from additivity in the relation between the retention of the sorbates and the composition of the eutectic. Thus, deviations from the relations governing the variation of the characteristics of the retention of the sorbate by the mixture of *p,p'*-azoxyanisole and *p,p'*-azoxyphenetole, caused by the formation of a eutectic, can be illustrated in relation to s-butylbenzene (Fig.1).

The study of the chromatographic characteristics of binary sorbents with low melting points and a high selectivity in relation to the *meta*- and *para*-isomers are of greater interest[35]. In the preparation of low-melting liquid-crystal mixtures the main component was *p,p'*-ethoxymethoxyazoxybenzene previously recommended for analytical purposes[33], having shown the maximum values $\sigma_H = 1.125-1.13$. The second component consisted of azoxyethers. Binary mixtures based on *p,p'*-ethoxymethoxyazoxybenzene with di-n-hexyloxyazoxybenzene proved to melt at lower temperatures than the main component. Furthermore, it has been shown that the fairly high selectivity, found for the first mixture and equal to 1.115, persists over a comparatively wide temperature range. Thus the use of a binary mixture of liquid crystals as the stationary phase ensures virtually the same selectivity in the separation of *m*- and *p*-xylenes as that of *p,p'*-azoxyphenetole and *p,p'*-ethoxymethoxyazoxybenzene usually employed for these purposes, but at a much lower temperature.

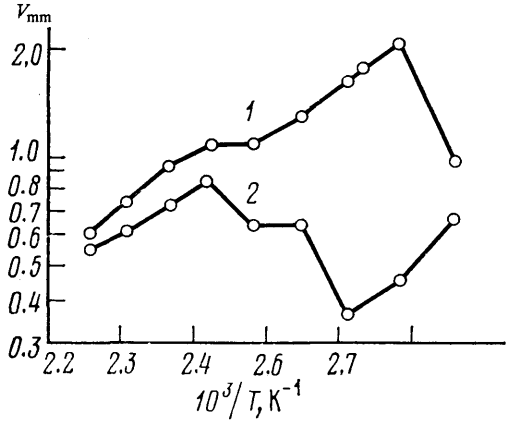


Figure 1. Dependence of the molar retention of s-butylbenzene on the reciprocal of the absolute temperature for a column with a eutectic mixture of *p,p'*-azoxyanisole and *p,p'*-azoxyphenetole[5]: *1*) experimental curve; *2*) curve plotted assuming the additivity of the retention volumes.

III. THE USE OF LIQUID CRYSTALS AS STATIONARY PHASES WITH A CONTROLLABLE SELECTIVITY

Numerous studies in the field of the above liquid crystal stationary phases showed that they are promising as universal sorbents with a controllable selectivity; this is an exceptionally important advance in the application of liquid crystals in gas chromatography in view of the usefulness of such compounds in all regions of their existance: solid, liquid-crystal, and isotropic liquid. Thus, when *p,p'*-azoxyphenetole is used, the chromatographic separation of s-butylbenzene and isobutylbenzene is attained only in the temperature range corresponding to the solid state of the stationary phase[45]. In the separation of cyclohexane and heptane it can also be valuable to ensure conditions corresponding to the solid crystal state of ethoxymethoxyazoxybenzene; the liquid-crystal region is best for the separation of heptane and iso-octane, as well as *m*- and *p*-xylenes, while the isotropic liquid phase of the substance is most selective in the separation of *p*-xylene from isopropylbenzene.

Thus the mesophase should not be regarded as a phase representing a single temperature range suitable for the analytical application of liquid crystals. In the possession of a single column with a liquid-crystal sorbent we have virtually as many stationary phases as the number of states characteristic of the given sorbent. Consequently liquid crystals, behaving as universal stationary phases can, on the one hand, greatly reduce the assortment of general purpose sorbents and, on the other hand, they can be employed for the solution of specific problems.

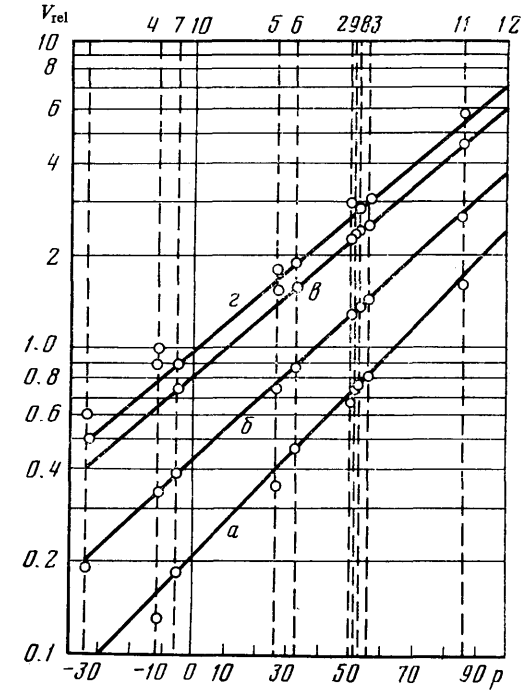


Figure 2. Dependence of the relative retention volumes of alkylbenzenes (on a logarithmic scale) on the conventional polarity of the stationary phases[80]: *1*) eutectic mixture of *p,p'*-azoxyphenetole and *p,p'*-azoxyanisole at 50 °C (SC); *2*) ditto at 100 °C (LC); *3*) ditto at 145 °C (IL); *4*) p-(n-heptyloxy)benzoic acid at 50 °C (SC); *5*) ditto at 100 °C (LC); *6*) ditto at 150 °C (IL); *7*) *p,p'*-azoxyphenetole at 110 °C (SC); *8*) ditto at 140 °C (LC); *9*) ditto at 170 °C (IL); *10*) squalane at 140 °C; *11*) poly(ethylene glycol)-2000 at 100 °C; *12*) 1,2,3,4-tetrakis(β-cyanoethoxy)neopentane at 140 °C; sorbates: *a*) benzene; *b*) toluene; *c*) *p*-xylene; *d*) *o*-xylene; notation: SC—solid crystal region; LC—liquid crystal region; IL—isotropic liquid.

1. The Conventional Chromatographic Polarity of Liquid Crystals

In order to estimate the selectivity of liquid-crystal sorbents in different phase states, the conventional chromatographic polarities were determined, by analogy

with Rohrschneider[90], by comparing the retention characteristics of the substances analysed (benzene, toluene, and *p*- and *o*-xylenes relative to n-nonane) on the test and standard sorbents. Fig.2 presents the relations between the logarithms of the relative retention volumes of the sorbates and the conventional chromatographic polarities of the stationary phases. *p,p'*-Azoxyphenetole, *p*-(n-heptyloxy)benzoic acid, cholesteryl cinnamate, squalane, and 1,2,3,4-tetrakis-(β-cyanoethoxy)neopentane were chosen as the stationary phases. Zero polarity was assigned to squalane at 140 °C and 100% polarity was assigned to 1,2,3,4-tetrakis-(β-cyanoethoxy)neopentane at the same temperature. Fig.2 shows that the conventional chromatographic polarity of the liquid crystal varies within wide limits with the phase transitions. In particular, for azoxyphenetole, it increases from -6 (the solid crystal region) to 50 (the anisotropic and isotropic liquid regions).

Thus, whereas in the fused state azoxyphenetole behaves as a moderately polar phase, below the melting point it functions as a non-polar sorbent, ensuring the elution of hydrocarbons virtually in accordance with their boiling points. The conventional chromatographic polarity can vary by 60 units for azoxyphenetole, by 40 units for the acid, and by 25 units for cholesteryl cinnamate. The intermediate values of the conventional chromatographic polarity can be obtained by using a compound column whose sections are filled with the same sorbents but operate at different temperatures. One of the authors of this review attempted to classify the liquid-crystal stationary phases in terms of the general classification based on the Rohrschneider polarity factors by introducing an additional factor *gf* characterising the *meta–para* selectivity of the mesophase[91]. The Rohrschneider equation then assumes the following form:

$$I = I_0 + ax + by + cz + du + es + gf,$$

where *a*, *b*, *c*, *d*, *e*, and *f* are the characteristics of the sorbate and *x*, *y*, *z*, *u*, *s*, and *g* are the characteristics of the sorbent; in particular *g* is the difference between the logarithmic retention indices of *m*- and *p*-xylenes. The following liquid crystals were investigated: *p,p'*-ethoxymethoxyazoxybenzene, *p,p'*-azoxyphenetole, and a binary sorbent consisting of *p,p'*-ethoxymethoxyazoxybenzene and *p,p'*-dibutoxyazoxybenzene[35]. For comparison, data for other stationary phases were also used[76,83,92,93]. It was shown that, in terms of the values of the linear analogues of polarity factors (*X*, *Y*, *Z*, *U*, *S*), the liquid-crystal stationary phases are sorbents of moderate polarity.

In the solution of many practical problems involving the separation of both a group of sorbates and individual positional isomers, it is necessary to select a liquid-crystal stationary phase which possesses fairly high values of the factor *g*, characterising the *meta–para* selectivity of the phase, and of the factor *x*, characterising the conventional chromatographic polarity. In this connection account was taken of the dependence of *g* on *x*, on the basis of which one can select the optimum stationary phase. Fig.3 shows that, although the binary sorbent based on a mixture of dinonyl phthalate and bentone-34 is characterised by a high selectivity in the separation of positional isomers ($g = 16.6$ units of the Kovats index), it is nevertheless a less polar sorbent ($x = 1.25$) than a liquid-crystal phase such as *p,p'*-ethoxymethoxyazoxybenzene ($x = 1.78$ and $g = 15.1$ units of the Kovats index).

The "conventional chromatographic polarity" of a liquid crystal changes abruptly in phase transitions, i.e. on passing from the solid to the liquid-crystal state and then to the isotropic state, increasing as a rule. Within the framework of the same phase state, "the conventional chromatographic polarity" increases with increasing temperature. As regards the *meta–para* selectivity, its magnitude is a maximum at the melting point and then monotonically decreases with increase of temperature. For example, when *p,p'*-azoxyphenetole passes from the solid state (100 °C) to the liquid-crystal state (140 °C), its polarity factor *x* increases from 0.1 to 1.9 units of the Kovats index, while the factor *g*, measured as the difference between the retention indices of *m*- and *p*-xylenes, increases from 2.5 to 14.8 units of the Kovats index. Within the limits of the liquid-crystal state, an increase of temperature from 140° to 150 °C entails a decrease of the *meta–para* selectivity of azoxyphenetole from 14.8 to 12.5 units of the Kovats index.

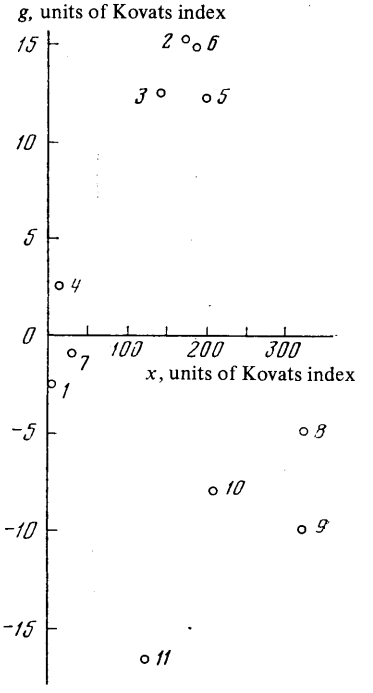


Figure 3. Dependence of the factor *g* on the polarity factor *x*.[91] Stationary phases: *1*) squalane; *2*) *p,p'*-ethoxymethoxyazoxybenzene; *3*) binary phase (*p,p'*-ethoxymethoxyazoxybenzene + *p,p'*-dibutoxyazoxybenzene); *4*) *p,p'*-azoxyphenetole, $t_c = 100$ °C; *5*) *p,p'*-azoxyphenetole, $t_c = 150$ °C; *6*) *p,p'*-azoxyphenetole, $t_c = 140$ °C; *7*) Apiezon L; *8*) PEG-4000; *9*) Rheoplex-400; *10*) Yucon-50NV-2000; *11*) binary phase (dinonyl phthalate + Bentone-34).

Thus the use of the above classification makes it possible to select stationary phases which, together with the extremum values of the factor *g*, have the necessary values of the other polarity factors. According to Herington[94], the selectivity in the separation of sorbates 1 and 2 is characterised by the ratio of their reduced retention times:

$$\sigma_s = t'_{R_2}/t'_{R_1} = (\gamma_1 p_1^0)/(\gamma_2 p_2^0),$$

where p_1^0 and p_2^0 are the vapour pressures of sorbates 1 and 2 and γ_1 and γ_2 are their activity coefficients in solution in the

stationary phase. This polarity index, which we mentioned previously, was used to estimate the *meta–para* selectivities of binary sorbents consisting of *p,p'*-ethoxymethoxyazoxybenzene and di-n-alkoxyazoxybenzenes[35], the influence of the vapour pressures and the activity coefficients of the sorbates (aromatic hydrocarbons–benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylenes) on the separation of the sorbates being estimated.

2. The Influence of Various Factors on the Structural Selectivity of the Liquid-Crystal Stationary Phases

The influence of various factors (temperature, pressure, and sorbate concentration) on the structural selectivity of the mesophase has been examined[95,96]. The temperature dependence of the structural selectivity of liquid-crystal stationary phases has been demonstrated in relation to azoxyethers. The maximum ratio of the retention characteristics of *p*- and *m*-xylenes is observed at the melting point of the liquid crystal and decreases monotonically as the clarification point is approached; above this point, xylenes are eluted as an overall peak. The temperature dependence of the *meta–para* selectivity in the liquid-crystal melt can be accounted for by the analogous dependence of the parameter *S*, which characterises the extent to which the molecules are arranged in parallel[3]; depending on the temperature, the value of *S* for the nematic phase varies in the range from 0.3 to 0.8, but, even at a temperature somewhat below the clarification point, the liquid crystal retains an appreciable tendency towards an ordered mutually parallel arrangement of molecular axes. The transition to the isotropic liquid is accompanied by an abrupt alteration of the sorption characteristics.

Kelker[2] recommends that one should work 2.3 K above the melting point of the substance (the reliability range). However, a detailed examination on the dependence of the retention parameters of the hydrocarbon analysed on temperature showed that there exists a broad region (5–6 K) with the maximum steric effect. Thus the ratio of the retention volumes of *p*- and *m*-xylenes on *p,p'*-azoxyphenetole is 1.096 at 134 °C, 1.10 at 136 °C, and 1.085 at 138 °C. This finding is important, since it shows that the liquid crystals used in gas chromatography do not require any special conditions for the maintenance of the column temperature, so that one can use ordinary commercial chromatographic apparatus. It has been shown that an increase in the concentration of the sorbate and in the carrier gas pressure in the column influence the *meta–para* selectivity in the same direction: the selectivity decreases with increasing concentration of the sorbate and the pressure of the carrier gas, the rate of decrease depending on the nature of both the liquid crystal and the carrier gas. This influence is associated with the breakdown of the ordered structure of the liquid-crystal melt as a consequence of the incorporation of the molecules of extraneous substances.

3. The Viscous Properties of Liquid Crystals

The low viscosity of nematic mesophases such as those of *p,p'*-azoxyanisole, *p,p'*-azoxyphenetole (1.47 cS), their eutectic mixture, and ethoxymethoxyazoxybenzene (3 cS) ensures high efficiency of the operation of chromatographic columns with the above sorbents.

4. Thermal Stability of Liquid Crystals

The use of liquid crystals as sorbents for gas chromatography requires the estimation of their volatility and thermal stability—factors which determine the upper temperature limit of the existence of the stationary phases. The upper temperature limits for the employment of a series of liquid-crystal stationary phases, determined by the derivatographic method, are 180 °C for *p,p'*-azoxyanisole, 200 °C for *p,p'*-azoxyphenetole, 195 °C for the eutectic mixture, 190 °C for *p*-heptyloxybenzoic acid, 270 °C for the ester of hydroquinone and *p*-(n-heptyloxy)benzoic acid, 220 °C for cholesteryl cinnamate, etc.[97,98]. Mention should be made of the work of Dewar and Schroeder[22] specially devoted to the synthesis of thermostable liquid-crystal compounds with high transition temperatures (among 19 new esters – *p*-phenylene alkoxybenzoates, *p,p'*-biphenylene-*p*-alkoxybenzoic acids, or *p*-alkoxycarbonylbenzoic acids - ten had mesomorphic regions extending over more than 90 K and the lowest transition temperature was 205 °C). Kelker et al.[19] studied high-temperature liquid-crystal sorbents. Investigations of the use of bis(*p*-methoxy-. *p*-butoxy-, *p*-hexyloxy-, *p*-phenylbenzylidene)-α,α'-bis-*p*-toluidines for the gas-chromatographic separation of polycyclic compounds[64,66–70] are instructive in this respect.

Naturally in many cases it is useful to carry out the chromatographic analysis at low temperatures, whence follows the necessity for seeking stationary phases in the state of the mesophase in the corresponding temperature range. An example of liquid crystals, with low melting points and clarification temperatures is provided by certain azo-compounds, azoxy-compounds, and azomethines[82,99,100], among which mention may be made of *p*-methoxybenzylidene-*p'*-butylaniline (the temperature range of the mesophase is from 21° to 47 °C), *p*-ethoxybenzylidene-*p'*-butylaniline (from 36 to 80 °C), and their eutectic mixture (from −16° to 50 °C).

Since the vapour pressure is of decisive importance in the estimation of the thermal stabilities of the stationary phases, the study[101] of the temperature variation of the vapour pressure of *p,p'*-azoxyanisole is of interest (Fig. 4).

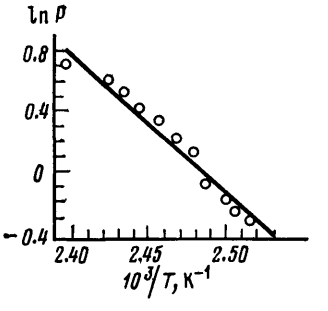


Figure 4. Dependence of the partial vapour pressure (mmHg) on the reciprocal of the absolute temperature[101].

The synthesis of high-temperature crystals holds out extremely great promise, because it extends the region of the analytical applications of mesophases in gas chromatography. Pitch mesophases constitute a fundamentally new type of high-temperature liquid crystals. They can be obtained in two ways: (1) by the carbonisation of coal and

petroleum tars; (2) by the joint carbonisation of individual organic compounds[102–106]. The formation of the liquid-crystal structure in the carbonisation of graphitisable substances is an irreversible process. The pitch mesophase obtained in the range 400–450 °C retains its liquid-crystal structure after complete setting and solidification[102,103]. Thus the temperature range of the existence of the pitch mesophase is much wider than in the other known systems. Brooks and Taylor[102,103] synthesised a series of pitch mesophases based on petroleum products and also by the joint carbonisation of organoelemental compounds and their mixtures (11 specimens); the analytical possibilities of these mesophases were also investigated and their likely usefulness in gas chromatography was demonstrated.

5. Dependence of the Efficiency of a Column with a Liquid Crystal Sorbent on Different Factors

The temperature dependence and the efficiency of a column containing a liquid-crystal sorbent have been studied by many investigators[46,49,79]. It has been shown that the efficiency decreases with decrease of temperature. Thus Fig. 5 presents the temperature variation[46] of the selectivity and efficiency of diundecyloxyazoxybenzene. When the above azoxyether is used for the separation of *m*- and *p*-xylenes at low temperatures, a "favourably" high value of σ_H and an "unfavourably" low value of HETP are obtained. A similar behaviour has been observed[49] in the separation of alkylnaphthalenes on *N*,*N*'-bis(*p*-methoxybenzylidene)-α,α'-bis-*p*-toluidine (BMBT). The authors determined the necessary number (*n*) of theoretical plates in the column for the separation of "difficult" pairs of alkylnaphthalenes on different stationary phases (Table 2).

Table 2.

Stationary phase	Pairs of alkylnaphthalenes*	*n*
Poly(phenyl ether)	1,4- and 2,3-DMN	
	2,3- and 1,5-DMN	85000
p,*p*'-Azoxyphenetole	2,3- and 1,2-DMN	92000
	1,3- and 1,4-DMN	42000
Graphitised thermal black	1,2- and 2,6-DMN	92000
	2,6- and 2,3-DMN	190000
N,*N*'-BMBT	1-EN and 2-MN	6500
	2-EN and 1,3-DMN	6500

*EN and MN = ethyl- and methyl-naphthalenes respectively and DMN = dimethylnaphthalene.

Grushka and Solsky[79,107,108] pointed out different changes in the height equivalent to a theoretical plate *H* as a function of the changes in temperature on a nematic liquid crystal. In particular, using *p*,*p*'-azoxyanisole as the stationary liquid phase on a capillary column[79], they noted the occurrence of temperature hysteresis of *H* (Fig. 6). *H* initially decreases with increasing temperature down to the melting point, where it increases sharply, falls again, and then rises once more in the nematic–isotropic transition. Two different values of *H* were obtained at the same temperature depending on whether the column was heated or cooled, the value of *H* being smaller in the cooling cycle than in the heating cycle. This conclusion is extremely important, since it indicates a high rate of mass transfer to the stationary phase in the cooling cycle (a clear-cut separation of *m*- and *p*-xylenes was in fact achieved in the supercooled region of azoxyanisole on a capillary column at 102 °C).

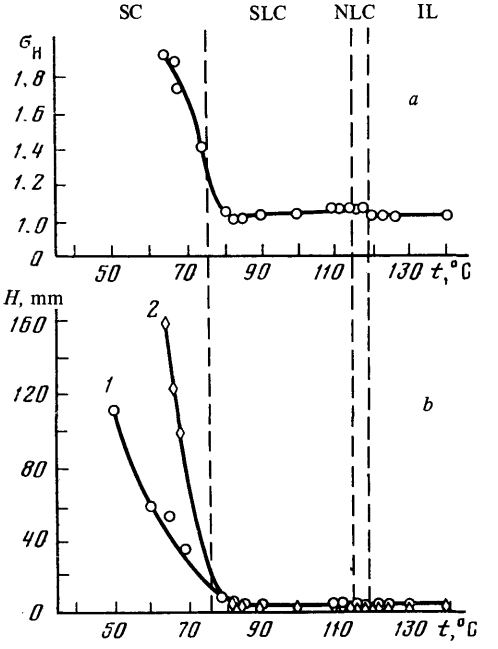


Figure 5. Temperature variation of the selectivity (*a*) and efficiency (*b*) of a column with *p*,*p*'-di-n-undecyloxyazoxybenzene[46]: *1*) *m*-xylene; *2*) *p*-xylene; SLC—smectic liquid crystal region; NLC—nematic region.

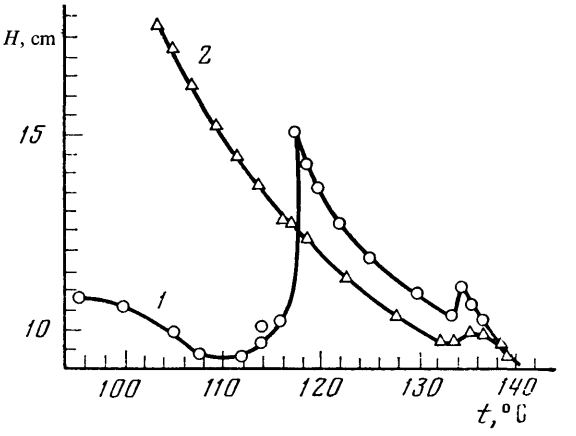


Figure 6. Temperature dependence of the height equivalent to the theoretical plate (HETP):[79] *1*) heating; *2*) cooling.

Grushka and Solsky[79] also showed that the minimum value of *H* is observed for lower flow rates of the carrier gas in the region of the mesophase; for example, in the case of *p*,*p*'-azoxyanisole on a capillary column the minimum value, H_{min}, is attained at a temperature of 120 °C, corresponding to the

liquid-crystal state, while at 90 °C (the solid crystal state of the substance) H_{min} has the same value, but is now obtained at higher carrier gas flow rates. H also decreases with decrease of the amount of stationary phase in the column. On a column with 0.1% of *p*-(*p*-ethoxyphenylazo)phenyl undecylenate (deposited on neutral glass grains), a lower value of H was obtained than on columns containing 0.27 and 0.69% of the stationary phase.

The possibility of the successful use of capillary columns with a liquid-crystal stationary phase has also been demonstrated in a study[40] whose authors used glass capillaries with a length between 8 and 27 m and 0.3 mm in diameter. Treatment of the capillaries with NaOH, NH_3, acids, HF, etc. did not lead to success, and only special treatment with EP-9 epoxy-resin ensured the complete impregnation of the capillary with the liquid crystal and the formation of an effective film. The epoxy-resin mixed with a hardener in proportions of 1:4 was dissolved in *o*-dichlorobenzene and a 10% solution was passed slowly through the capillary with the aid of a water pump. In addition 15 ml of *o*-dichlorobenzene was introduced, after which the capillary was dried at 120 °C in a stream of argon. The liquid-crystal compound was then dissolved in a suitable solvent and was introduced into the capillary by the piston method. The film of the liquid crystal within the capillary was dried in a stream of argon at a slowly rising temperature.

In their study of the retention of sorbate molecules on polymeric sorbents modified with liquid crystals, Zelenkova et al.[109] also showed that the HETP decreases with increase of temperature and with decrease of the amount of the stationary phase. The greatest increase of the sorbent efficiency is observed when 5–20% of the liquid crystal is deposited on the polymeric sorbents.

6. The Influence of the Impregnation of the Carrier

The optimum amount of the stationary phase, deposited on a solid carrier, is determined by the influence of a number of competing factors associated with the selectivity, efficiency, and duration of the analysis. Low degrees of impregnation of the carrier, which make it possible to reduce the HETP and to shorten the duration of the analysis, are preferable. However, in order to obtain exact and reproducible retention parameters (particularly when these are to be used for the calculation of the thermodynamic functions of dissolution), the amount of the stationary phase must be sufficient to achieve the complete coverage of the carrier and to eliminate the distorting influence of adsorption on the surface of the solid.

The influence of the molecular packing density of the test substance on the dependence of the retention parameters on the amount of the stationary phase and also the influence of the solid carrier on the selectivity of the liquid-crystal stationary phase was demonstrated by Gabitova and Vigdergauz[110] for azoxyethers in the separation of *m*- and *p*-xylenes and aromatic and paraffinic compounds using columns with different contents of the stationary phase.

Fig.7 presents the variation of the specific retention volume of toluene on *p,p'*-azoxyphenetole with the degree of impregnation in different phase states. The nature of the curves shows that the contribution of adsorption factors to the retention of sorbates by isotropic and anisotropic liquids is negligibly small for a degree of impregnation exceeding 10%, i.e. above this value the retention parameters are almost independent of the amount of the stationary phase. On the other hand, in the solid crystal state the retention is naturally determined by the area of the adsorbing surface and, since the latter depends only slightly on the amount of the stationary phase, the specific retention volume is inversely proportional to the degree of impregnation V_g. The results permitted the determination of the lower limit of the possible amount of the liquid-crystal stationary phase. They demonstrated a relation between the jump in the retention parameters at the melting point and the degree of their impregnation, while at the clarification point the jump is determined solely by the nature of the substance analysed. Furthermore it has been shown that (1) with decrease in the degree of impregnation the *meta–para* selectivity of the liquid-crystal sorbent diminishes and (2) the temperature of the transition of the stationary phase from the solid state to the liquid-crystal state decreases with decrease in the degree of impregnation.

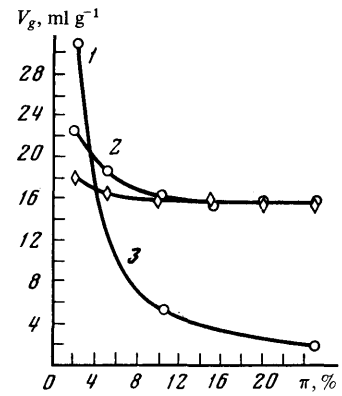


Figure 7. Dependence of the absolute specific retention volume of toluene on the amount of *p,p'*-azoxyphenetole (% relative to the mass of Chromosorb P) at different temperatures (°C): *1*) 100; *2*) 140; *3*) 170.[80]

The principal studies with liquid-crystal sorbents in gas chromatography have been carried out in columns using virtually inert solid carriers which have a specific porosity, are mechanically stable, and have a specific surface of ~10 $m^2 g^{-1}$. The use of liquid crystals deposited in the form of a monolayer on an active solid carrier—macroporous Silochrome with a high specific surface—has been described recently[43,44]. It has been shown that the use of thin, nearly monomolecular layers of nematic and smectic as well as cholesteric stationary phases leads to the observation of a fairly high *meta–para* selectivity and to a shift of the selectivity maximum towards lower temperatures relative to those corresponding to the usual impregnation process (i.e., as in the studies of Serpinet[111,112], a change in the phase transition temperature is observed). Apparently when a monolayer is employed, the support plays an extremely active and possibly a decisive role in the separation of the substances analysed.

The role of an active sorbent with a high surface area in the gas-chromatographic separation of mixtures has been demonstrated by Averin et al.[47], who increased the efficiency of the separation and reduced the temperature of the separation process at high concentrations of the substances analysed by employing an active adsorbent

(Silochrome) impregnated with a liquid-crystal stationary phase (azoxyphenetole) in the separation *m*-, *p*-, and *o*-isomers of vinyltoluene and noted a further series of advantages of this method of separation. In this connection one must also mention studies[109,113] in which polymeric sorbents, such as Polysorb-1 and Chromosorb-101 modified with liquid crystals, for example *p,p'*-azoxyphenetole and *p,p'*-ethoxymethoxyazoxybenzene, were used for the gas-chromatographic separation of various classes of organic compounds—paraffinic and aromatic hydrocarbons, alcohols, ketones, aldehydes, acids, lactones, etc., aromatic compounds being retained on these sorbents more tenaciously than paraffinic hydrocarbons. The separation of *o*- and *m*-xylenes, *o*- and *m*-cresols, etc. has been achieved[109,113], while the *m*- and *p*-isomers were not separated. The influence of the amount of the azoxyphenetole liquid crystal on the principal characteristics of the gas-chromatographic process, on the corrected retention volumes V_R of the sorbates, on the HETP, and on the asymmetry coefficient has been investigated.

The influence of the nature of the solid carrier on the chromatographic behaviour of the mesophase has been noted[79,107,108]. The authors of these investigations suggest that the anomalous effects [the influence of the rate of heating of the liquid crystal on its melting point, the time dependence of the coefficients *K* (the partition coefficient of the sorbate) and the HETP (the efficiency of the separation) near the melting point, the form of the variation of the retention parameters for two ways of varying the temperature in experiments using the capillary column[79] and glass grains of different types[107,108] as the solid carrier] can be explained by the influence of surface orientational forces of the carrier and the inner wall of the capillary tube. Furthermore, it has been shown that the nature of the orienting of the molecules of the liquid crystal on the surface of glass grains is determined by the extent of the diffusion of the sorbate molecules, i.e. the diffusion of solutions in which the molecules of the liquid crystals are oriented parallel to the surface of the glass grains is usually more extensive than the diffusion of solutions with a perpendicular arrangement of liquid crystal molecules on this surface.

The influence of the surface of the solid carrier on the thermodynamic functions of the dissolution of substances has been studied[30,114]. The absence of effects at the solid–liquid crystal interface and the occurrence of only very weak interactions in the gas–liquid crystal system, which can be neglected for a film thickness of at least ~1000 Å, has been demonstrated.

7. The Influence of an Electric Field on the Selective Properties of Liquid Crystals

Under the influence of an electric or magnetic field, the degree of order among the molecules of the liquid crystal changes in the region of the mesophase[115], which leads in its turn to an alteration of the retention characteristics of the substances analysed. In 1963 one of the authors of this review suggested that the chromatographic process be carried out in an electromagnetic field[116]. Under the influence of the field, the molecules of the stationary liquids (and in many instances also the components being separated) are polarised and their sorption properties are therefore altered. Evidently the introduction of an additional factor into the chromatographic process should increase the scope for controlling the selectivity of the stationary phase and permit the study of a new range of sorption phenomena.

The relevant investigations have been carried out by Taylor and coworkers[117–119] using short capillary columns containing mixtures of cinnamate esters and cholesteryl myristate as the stationary phases. An electric field up to 500 V was applied to the column by means of external electrodes attached by means of a special paste and aluminium foil. The authors investigated the dependence of the shape of the peaks and retention times of hydrocarbons and oxygen-containing compounds on the electric potential, its frequency, the analytical temperature and the content of the stationary phase. Application of an electric field increased the retention times of the substances analysed and the peaks became more symmetrical.

Vigdergauz and coworkers[120,121] investigated the influence of an electric field on the chromatographic retention of diethyl ether, acetone, ethyl methyl ketone, n-hexane, heptane, cyclohexane, and benzene, by a liquid-crystal stationary phase—cholesteryl laurate at 86 °C. The length of the spiral column designed by Taylor et al.[117] was 10 m and the potential applied to the electrodes was 500 V. In order to estimate the effect of the electric field, the difference between the free energies of sorption of the test substances $\delta(\Delta F^0)$ in the presence and absence of the field was calculated:

$$\delta(\Delta F^0)\ \text{cal mol}^{-1} = RT \ln \frac{\Gamma'_{500}}{\Gamma'_0} = 714 \ln \frac{\Gamma'_{500}}{\Gamma'_0},$$

where Γ'_{500} and Γ'_0 are the partial Henry coefficients for the sorbates in the presence and absence of the field respectively [$\Gamma' = (t_R/t_0) - 1$, where t_R and t_0 are the retention times of the sorbate and the non-sorbed substance respectively].

The results of the calculation permitted the conclusion that $\delta(\Delta F^0)$ can reach 400–500 cal mol^{-1}, which corresponds, in absolute magnitude, to the value of $\delta(\Delta F^0)$ for the transition from the isotropic liquid to the mesophase[5] and also to the values of $\delta(\Delta F^0)$ for neighbouring homologues, i.e. 100 units of the Kovats index. The use of the above effect for analytical purposes is possible only after the development of a column design ensuring an adequate efficiency. The results justify the hypothesis that, together with familiar external factors such as temperature and pressure, the application of an electric field can also be used for the specific regulation of the selectivity of the chromatographic column.

The following features of the data described above on the analytical application of liquid crystals must be noted:

(1) Despite the fact that extensive studies have been made on the utilisation of liquid-crystal sorbents in gas chromatography, the general characteristics relating the chromatographic selectivity to the structure of the liquid crystal have not so far been discovered[122–124].

(2) The majority of the liquid crystals investigated are designed for the solution of the narrow problem of the separation of *meta*- and *para*-isomers and exhibit a weak group selectivity. Consequently one must direct attention to the synthesis of mesophases exhibiting both specific and general selectivity.

The question arises of the requirements which must be met in the synthesis of liquid-crystal stationary phases:

(a) These must be liquid crystals of the nematic type. The wide-scale employment of smectic liquid crystals will become possible only in the case of very high selectivity. The introduction of new stationary liquid-crystal phases into chromatographic analysis is justified only in those cases where these phases have a significant advantage.

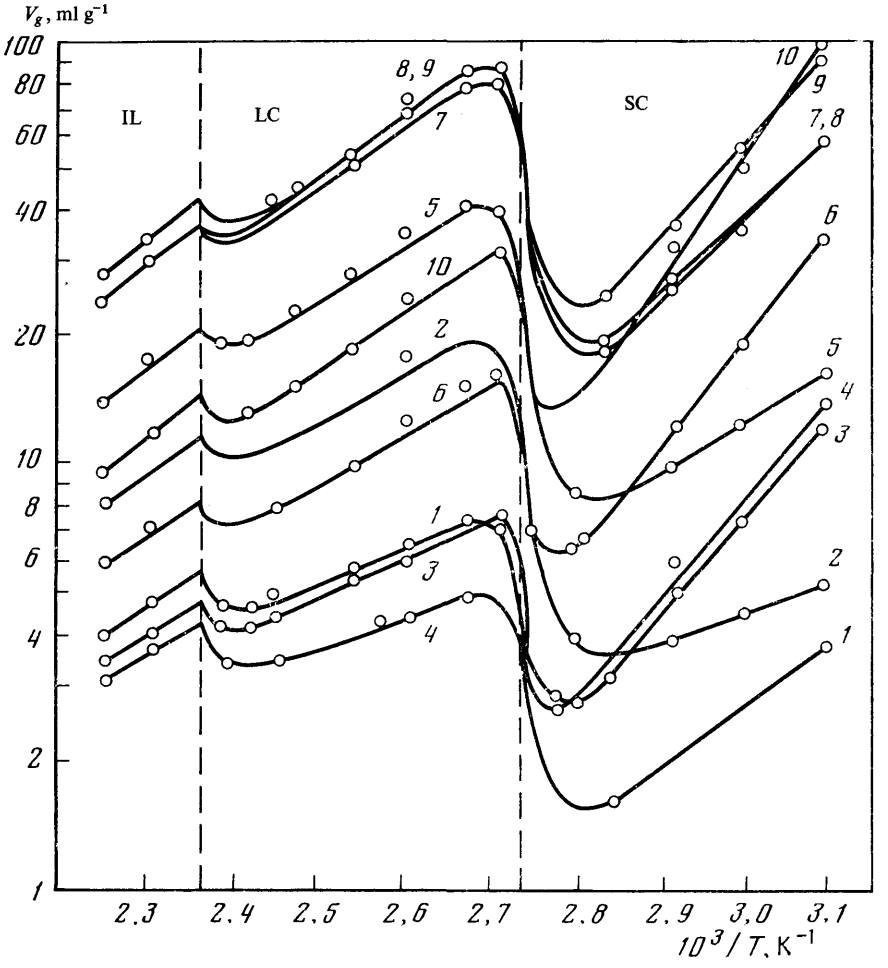


Figure 8. Dependence of the specific retention volumes of hydrocarbons on the reciprocal of the absolute temperature of a column with *p,p'*-ethoxymethoxyazoxybenzene[46]: *1*) cyclohexane; *2*) benzene; *3*) heptane; *4*) iso-octane; *5*) toluene; *6*) octane; *7*) *m*-xylene; *8*) *p*-xylene; *9*) isopropylbenzene; *10*) nonane.

(b) The liquid crystal synthesised must contain highly polar functional groups. Certain examples have been described[125–127], but the analytical scope of such liquid crystals has not so far been estimated. Unfortunately the liquid-crystal stationary phases already investigated are phases of moderate polarity or in practice one has to deal with the separation of a multicomponent mixture consisting of compounds of different classes.

(3) Liquid-crystal stationary phases must have a wide and controllable temperature range of the mesophase. It can be extended either by synthesising the appropriate liquid-crystal compound or by using mixed phases forming a eutectic. The majority of the liquid crystals synthesised are medium-temperature stationary phases the range of the existence of the mesophase of which extends up to 200 to 300 deg. Hence follows the interesting problem of the synthesis and utilisation of the high-temperature phases—the so-called pitch mesophases.

(4) The study of the influence of field effects (electrical and magnetic) on the chromatographic processes in a sorbate–liquid crystal system is of very great interest.

IV. CHROMATOGRAPHIC STUDY OF THE PHASE TRANSFORMATIONS OF LIQUID CRYSTALS

The retention volume and the corresponding retention time (V_R and t_R) in gas chromatography are fundamental characteristics of the sorbate. Fig.8 presents the relations between the logarithm of the specific retention volume and the reciprocal of the absolute temperature of the column containing ethoxymethoxyazoxybenzene[46]. The retention parameters of the substances analysed are extremely sensitive to phase transitions of the sorbent as a consequence of which the plot clearly reveals three regions of its phase state: solid, liquid-crystal, and isotropic liquid. The phase transitions are accompanied by sharp changes in the retention parameters. Under these conditions, the retention volumes increase at the melting point by a factor of 4–10 and at the clarification temperature by 15–20%. The melting point, clarification temperature, and transition temperature between different mesophases are characterised by an abrupt alteration of the retention parameters; on the other hand, there are cases where

there is no maximum, for example, when *p*-phenylene bis-*p'*-(n-heptyloxy)benzoate passes from the solid state to the smectic mesophase, which is due to the high viscosity of the latter[5,83].

Within the framework of the same temperature range between the phase transition temperatures, there is a gradual decrease of the retention volumes as the temperature rises. The transition from the solid to the liquid-crystal state leads to a change of the overall selectivity, which is expressed by an inversion of the elution sequence of aromatic, naphthenic, and paraffinic hydrocarbons. The same relations determining the temperature variation of the retention were observed by Kelker[15] for *p,p'*-azoxyphenetole, by Dewar and Schroeder[16] for *p,p'*-di-n-hexyloxyazoxybenzene, and by Barrall et al.[24] for cholesteric liquid crystals. In particular, Barrall et al.[24] noted that the elution times of the sorbates increase by a factor greater than 3.5 on transition from the cholesteric mesophase to the isotropic liquid.

Further studies demonstrated that there is a more complex relation between the retention and temperature. Thus, when the solid-crystal phase of ethoxymethoxyazoxybenzene is heated[33] and its isotropic liquid phase is cooled in the range 70–100 °C, hysteresis is observed, i.e. the retention of the sorbates and the selectivity of their separation are linked to the "memory" of the column. Other workers have also observed hysteresis[49,79].

The high sensitivity of the sorption characteristics and the associated retention parameters of the substances analysed to the phase state of the sorbent permits the solution also of the converse problem—the determination of the phase transition temperatures and also of the accompanying structural changes with the aid of chromatographic apparatus. This advanced gas chromatography to the forefront of the effective methods for the investigation of physicochemical properties and phase transformations in liquid crystals[24]. The likely usefulness of the combined study of phase transitions in liquid crystals by thermography and a combination of gas chromatography and the thermo-optical method was first demonstrated by Vigalok and coworkers[46,85].

Fig. 9 presents the thermo-optical curve for the dependence of the logarithm of the retention of hydrocarbons on the reciprocal of the temperature of the column with *p,p'*-heptyloxyazoxybenzene and a thermogram of this substance. The graphical data demonstrate the full agreement within the limits of 1–2 K of the phase transition temperatures determined by all three methods: sorption, optical, and thermal, despite the fact that the principle of each is different. As regards the additional information which can be obtained with the aid of chromatography, one should note the possibility of the study of the prefusion process and the accompanying structural changes in the crystal as well as a quantitative estimate of these changes (Kelker[20] pointed out earlier the occurrence of prefusion effects in liquid crystals which were treated by various investigators either as homogeneous processes or as processes involving heterogeneous fluctuations[128,129]).

Using a combination of the chromatographic and thermo-optical methods, the phase transitions in binary liquid-crystal sorbents have also been determined. It has been shown that the greatest shift of the phase transition temperature towards low values, amounting to 30 K, has been observed for the eutectic mixture of *p,p'*-ethoxymethoxyazoxybenzene and di-n-butoxyazoxybenzene, while the corresponding shift for the mixture with di-n-hexyloxyazoxybenzene amounts to 18 K.[35] The phase transition temperatures can also be determined by differential scanning calorimetry combined with gas–liquid chromatography (GLC).[30]

The idea of nematic order in poly(vinyl chloride) has been confirmed by chromatographic studies[130]. It has been shown that the nature of the separation of the *cis*- and *trans*-decalins differs markedly in the experimental temperature range (35–170 °C) and that the elution sequence of the isomers undergoes inversion as a function of the phase state of the sorbent.

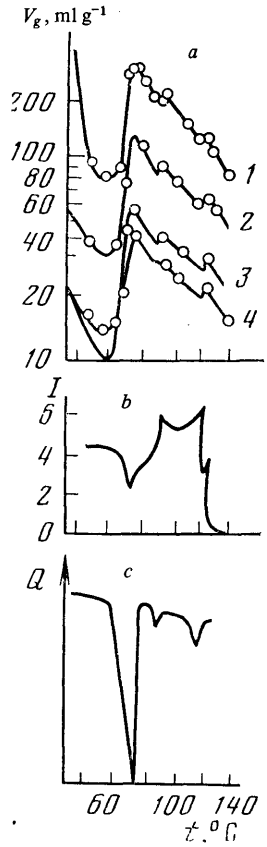


Figure 9. Chromatographic (*a*), thermo-optical (*b*), and thermographic (*c*) curves for *p,p'*-heptyloxyazoxybenzene[46]. Sorbates: *1*) *p*-xylene; *2*) toluene; *3*) n-pentane; *4*) benzene.

V. THERMODYNAMICS OF THE SORPTION OF SUBSTANCES BY LIQUID CRYSTALS

The possibility of the analytical and preparative separation of compounds with similar boiling points by chromatography in a gas–liquid crystal system is due to the significant differences between the thermodynamic functions of the sorption of isomeric compounds by liquid crystals. Gas chromatography is therefore an effective method for the investigation of the properties of the solvent and the behaviour of the solute in the liquid crystal, as well as the determination of the thermodynamic parameters of mesophases; one can then determine from chromatographic data the thermodynamic parameters under conditions close to infinite dilution, where no disruption of the structure of the liquid-crystal phase is observed[29,30,48,114,131–136]. Furthermore, the absence of an influence on the accuracy of the

determination of the thermodynamic parameters by effects on the solid–liquid crystal and gas–liquid crystal interfaces for a thickness of the liquid crystal film of ~1000 Å was noted above.

On the basis of the analysis of the activity coefficients γ^{∞} of the sorbates at infinite dilution, a molecular theory of the solubility of substances in liquid crystals has been developed[135]. The activity coefficients have been interpreted at the molecular level by means of statistical mechanics. As usual, the thermodynamic calculations are based on the determination of the specific retention volume V_g.

In their study of the effects of the dissolution of xylenes in cholesteryl myristate, which can exist in the state of both smectic and cholesteric mesophases, Martire et al.[29] established that only the smectic phase gives rise to the selective separation of *m*- and *p*-xylenes. Kelker[18] also pointed out the absence of selectivity in the cholesteric phase, while Vetrova and coworkers[43,44] achieved a fairly clear-cut separation of *m*- and *p*-xylenes on cholesteryl pelargonate deposited in a monolayer on an active adsorbent. Unfortunately, the authors of the present review were unable to reproduce these results.

Jeknavorian and coworkers[139,140] derived the same relations for the solubilities of the above compounds in liquid-crystal sorbents as Chow and Martire[135] on the basis of an analysis of the activity coefficients for the dissolution of n-alkanes and aromatic hydrocarbons, including xylenes and *cis*- and *trans*-isomeric alkyl cyclohexyl ethers on the *p*-(*p'*-ethoxyphenylazo)phenyl heptanoate nematic liquid crystal.

The phase transition temperatures are known to be preceded by pretransformation periods. Kelker and coworkers[20,21] showed that the effects preceding the phase transitions can be investigated by chromatographic methods; azoxyethers (azoxyanisole, azoxyphenetole, and their eutectic mixtures) can be investigated by chromatographic methods. Prefusion processes have been described[128,129]. Pretransition effects have also been demonstrated by measurements of viscosities[141], specific heats[142], coefficients of linear expansion of NMR signals[143], and infrared spectra[144]. Bauer and Bernamont[145] found in relation to *p,p'*-azoxyanisole that the pretransformation period occurred ~10 K below the clarification temperature. To account for the pretransition effects, Kelker used the molecular-statistical theory developed by Tsvetkov[146], Weber[143], and Maier and Saupe[147]. The pretransition behaviour of nematic phases can be described also with the aid of the Frenkel's two-phase concept[148].

The thermodynamics of the dissolution of substances in liquid crystals has been studied[42] by capillary gas chromatography. On the basis of the molecular theory of solubility[135], the authors investigated the influence of the length of the alkyl chains in the homologous series of liquid-crystal ketoximes on the molar enthalpy Δh^0 and entropy Δs^0 of the solution and the excess functions of the dissolution of the above substances.

It has been shown[42] that the partial molar enthalpies and entropies of all the sorbates (alkanes, aromatic hydrocarbons, xylenes, and disubstituted benzenes) exhibit a clear alternation in the homogous series of ketoximes with inversion at the clarification temperature. Compounds with an even number of carbon atoms had lower values of Δh^0 and Δs^0 at a higher clarification temperature. The disubstituted benzene isomers used as sorbates were fully separated and the *p*-isomers exhibited higher values of Δh^0 and lower values of γ^{∞} in the region of nematic liquid crystals.

The thermodynamic functions of the sorption of different sorbates on liquid crystals have been studied by Vigdergauz and coworkers[5,26,83,85,88]. Calculations showed that the transition from the anisotropic to the isotropic region is accompanied by an increase of the heat of sorption and that, whereas in the isotropic region the values of Δh for the isomers are similar, in the case of the mesophase there are significant differences due to the molecular structure of the sorbates.

Kelker showed for alkylbenzenes[15] that the heat of mixing of xylenes with *p,p'*-azoxyphenetole is an order of magnitude higher than the heat of mixing with the usual stationary liquids. Thus, the heats of mixing of *o*-xylene with the azoxyphenetole mesophase, benzylbiphenyl, and 7,8-benzoquinoline are 5400, only 520, and 850 cal mol^{-1} respectively. The heat of mixing is always higher by ~3000 cal mol^{-1} in the mesophase than in the isotropic liquid; consequently the dissolution process in an anisotropic composition requires more energy, i.e. the dissolution of substances in both the liquid-crystal and isotropic regions of the sorbent is accompanied by the adsorption of heat and the mesophase is more endothermic in all instances apart from the eutectic mixture.

The corresponding difference for *p,p'*-azoxyphenetole[83,85] amounts to 2–3 kcal mol^{-1}, which agrees with the data of Kelker[15], who, however, used in the calculation the latent heats of vaporisation λ at the boiling points of the sorbates and not at the column temperature. The change in the degree of endothermicity on transition from the isotropic liquid to the mesophase decreases for *p*-(n-heptyloxy)-benzoic acid, the ester of hydroquinone and *p*-(n-heptyloxy)-benzoic acid, and cholesteryl cinnamate to 0.5–1 kcal mol^{-1}, while in the case of the eutectic mixture the corresponding difference for paraffins is close to zero and for the remaining alkylbenzenes and cycloparaffins it amounts to ~1 kcal mol^{-1}.

Comparison of the heats of sorption and the excess enthalpies of mixing with those observed in the case of the isotropic phase and the mesophases (smectic and nematic) of the ester of hydroquinone and heptyloxybenzoic acid showed that the smectic region is the most endothermic: $\Delta h \cong 4$ kcal mol^{-1} (in the nematic region $\Delta h = 1.2$–2.3 kcal mol^{-1}) The results can be accounted for by the higher degree of order in the structure of the smectic region, so that the penetration of extraneous molecules into the mesophase of the smectic liquid crystal requires a greater expenditure of energy than in the case of the nematic state. For anisotropic melts of azoxyphenetole, the entropy of mixing Δs is greater by 8–10 e.u. than for the isotropic phase.

Thus the transition of the sorbent to the liquid crystal region is accompanied by a sharp change of both the entropy of mixing of the sorbate with the stationary liquid (which corresponds to an abrupt alteration of the retention characteristics in the temperature range of the phase transition) and of the enthalpy of mixing (which corresponds to a dependence of the logarithms of the retention characteristics on $1/T$). The set of these changes ensures extensive possibilities for the regulation of the selectivity in the separation of mixtures incorporating isomers with similar boiling points.

As already mentioned, a considerable scope for the regulation of selectivity arises from the use of mixed stationary phases[5,26,35,88]. The nature of the intermolecular interaction in such a system depends on whether the binary system includes one or two liquid-crystal compounds, on whether they form a eutectic mixture, and on the type of mesophase of the mixed liquid-crystal ingredients. It is noteworthy that the absolute difference between the heats of sorption of the substances analysed in the isotropic and anisotropic regions on the individual sorbents is greater than on the mesophase. This effect had been noted earlier by Kelker[2] in relation to *o*-xylene

and shows that the mixing process is accompanied by a change in the energy of the system. The excess free energy of the mixed phase $\Delta f'$ can be calculated on the basis of published data[149,150] from the formula

$$\lg V_{mm} = x_1 \lg V_{mm1} + (1-x_1) \cdot \lg V_{mm2} + \Delta f'/4.57T,$$

where $V_{mm} = V_g M/22400$ is the molar retention, x_1 the mole fraction of the individual phase in the mixture, T the column temperature (K), and M the molecular weight of the stationary phase.

For the sorbates investigated, the above relation is represented by curves with a maximum corresponding to the 60 : 40 eutectic mixture; the maximum value of $\Delta f'$, calculated from the dependence of the molar retention on the phase composition, then corresponds to 100 °C, i.e. a temperature close to that of eutectic fusion (Fig. 10). The effective value of Δf, obtained for a 10% degree of impregnation of Chromosorb on the basis of the retention characteristics of n-paraffins, proved to be 630–640 cal mol^{-1}. The value of $\Delta f'$ calculated from the retention characteristics of polar compounds are significantly greater, since they include the energy of the specific interaction of the sorbate with the eutectic.

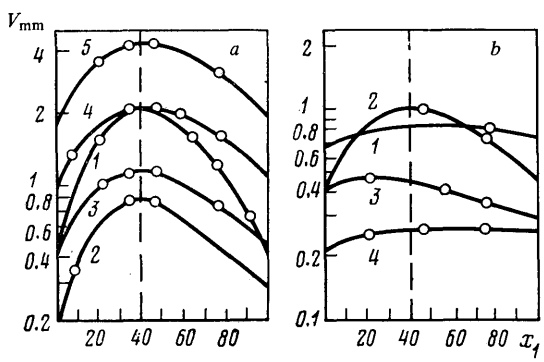


Figure 10. Dependence of the molar retention of sorbates (on the logarithmic scale) on the content of p,p'-azoxyphenetole x_1 in its mixture with p,p'-azoxyanisole[5]. The dashed lines correspond to the eutectic mixture: *a*) retention of s-butylbenzene (curve *1*), butyl acetate (curve *2*), n-decane (curve *3*), n-undecane (curve *4*), and n-dodecane (curve *5*) at 100 °C; *b*) retention of n-decane at different temperatures (°C); *1*) 90; *2*) 100; *3*) 140; *4*) 170.

The excess free energies of mixing of the individual components $\Delta f'$ (from the data for n-paraffins) as well as the values of $\Delta f'$ characterising the additional energy of the interaction of xylenes with binary solvents were calculated for binary systems incorporating p,p'-azoxyphenetole (I), p-(n-heptyloxy)benzoic acid (II), p-phenylene bis-p'-(n-heptyloxy)benzoate (III), cholesteryl cinnamate (IV), poly(ethylene glycol)-2000 (V), and squalane (VI).[5,88]

In the first place the determination of the dependence of $\Delta f'$ and $\Delta f''$ on the composition of mixtures of p,p'-azoxyphenetole with poly(ethylene glycol) and squalane permitted the conclusion that the values of the calculated functions are determined by the phase state of the liquid-crystal ingredient. Thus, whereas at temperatures of 170° and 190 °C corresponding to the isotropic liquid state the values of $\Delta f'$ are virtually the same (Table 3)[88], transition to the temperature at which the mesophase exists (140 °C) entails an increase of $\Delta f'$ by 400 cal mol^{-1}. A negative value of $\Delta f''$ for xylenes has been observed in the case of the p,p'-azoxyphenetole–squalane pair, which is characterised solely by the dispersion interaction between the components.

Table 3. Experimental values of $\Delta f = \Delta f' + \Delta f''$ (cal mol^{-1}) for binary systems of phases[88].

Sorbates	(I)–(V) 140° C	(I)–(V) 170° C	(I)–(V) 190° C	(I)–(VI) 140° C	(I)–(II) 136° C	(II)–(III) 100° C	(III)–(IV) 156° C
n-Paraffins	560	150	140	770	270	520	—160
m-Xylene	730	310	300	450	260	800	—120
p-Xylene	320	320	320	400	260	830	—110

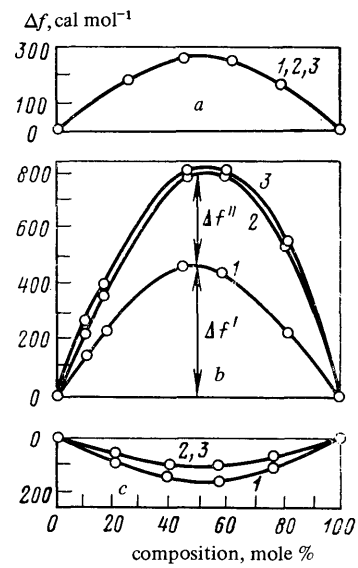


Figure 11. Dependence of the quantity $\Delta f = \Delta f' + \Delta f''$ on the composition of a binary liquid crystal phase[88]. Systems: *a*) (I)–(II); *b*) (II)–(III); *c*) (III)–(IV). Sorbates: *1*) n-paraffins ($\Delta f'$); *2*) *m*-xylene; *3*) *p*-xylene.

The values of $\Delta f'$ for the liquid-crystal mixtures (I)–(II) and (II)–(III) are positive, while those for the (III)–(IV) mixture are negative. One cannot rule out the possibility that the latter is associated with the transition of the entire (III)–(IV) system to the state of a cholesteric mesophase (by analogy with Friedel's data[151]). Fig. 11 presents relations between Δf and the composition of a binary liquid-crystal phase. Evidently in the (I)–(II) system the curves corresponding to n-paraffins and xylenes coincide. This indicates an additive variation of the selectivity in the separation of xylenes as a function of the composition of the phase and the absence of additional specific interactions ($\Delta f'' = 0$). The coincidence of the curves corresponding to

xylenes in the (III)–(IV) system is a consequence of the virtual absence of selectivity in both components of the mixed phase at the temperature of the measurement. In the (II)–(III) system an anomalous increase of selectivity is observed with a maximum corresponding to an ether content of 10 mole %. This composition of the mixed phase yields a ratio of the retention volumes of *p*- and *m*-xylenes of 1.065–1.070, while for the individual phases (II) and (III) the ratios are respectively 1.05 and 1.02.

* * *

During the period when the manuscript was with the editors, a number of studies devoted to various theoretical and applied aspects of chromatography in the gas–liquid crystal system were published. The separation of structural isomers of various substituted dialkylbenzenes has been achieved[152–159] on columns with mesophases containing azo- and azoxy-groups. The isomeric dimethylnaphthalenes have been analysed[160–162] and polycyclic aromatic hydrocarbons, in particular anthracene, phenanthrene, benzo phenanthrene, benzopyrenes, and perylene have been investigated[160–165]. Substances of biological origin—cholic acids and their derivatives, steroids, and phenolic metabolites of benzo[*a*]pyrene—have been investigated with the aid of high-temperature nematic liquid-crystal phases[166,167]. In addition enzymes have been analysed[168] and enantiomeric *N*-pentafluoropropionamides have been separated on smectic mesophases[169]. Problems of the influence of the solid carrier on the chromatographic characteristics of liquid-crystal stationary phases have been studied[154,160,170–172] and a number of investigations have been devoted to the thermodynamics of the dissolution of sorbates in mesophases[173–176].

The study of the influence of an electric field on the separating capacity of liquid crystals has been continued[177] and capillary columns have been used[164,178].

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Electronic Processes Induced by Radiation in Solid Organic Systems

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We shall discuss the behaviour of charged particles produced by radiation and their role in physical and chemical processes (e.g. electrical conduction, recombination luminescence, and various optical properties). By analysing existing physico-chemical theories and concepts we can describe these processes quantitatively (at least to a first approximation) as well as gaining a deeper understanding of their mechanism. 402 references.

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I. INTRODUCTION

The fundamental importance of ion–molecule reactions during the radiolysis and photolysis of condensed phases was demonstrated during the late 1960's.[1-4] In particular, detailed studies were made of the electrical phenomena accompanying the radiolysis of hydrocarbons[1,5], such as induced electrical conductivity, recombination luminescence, and thermally stimulated and photo-stimulated processes in low-molecular hydrocarbon glasses previously irradiated at low temperatures. Since that work was reported much progress has been made in understanding the role of charged particles (and especially electrons) in the radiolysis of liquid, non-polar molecular systems[6,7], and the mobility and reactivity of excess electrons in liquid hydrocarbons have been fully investigated[8,9].

We have used the results of experimental and theoretical studies of organic (and inorganic) liquids to analyse the electronic processes induced by radiation in solid organic systems such as glasses and polymers. In this review we shall examine the experimental (and, to a lesser extent, the theoretical) work on charge generation, stabilisation, and recombination mechanisms which has been published since the end of the 1960's, as well as studies of charge transfer under the influence of an external or an internal (coulombic) electric field in solid organic systems. By analysing this information we have been able to assess the current level of understanding of these problems and to identify the topics to which more attention should be devoted.

II. CHARGE GENERATION

In this Section we shall discuss the theories by which the yield of free charges (and of charges contributing to electrical conduction) may be calculated for the radiolysis or photolysis of organic materials in a condensed phase with

allowance for the energy spectrum of the secondary electrons. This treatment explains both the changes in electrical conductivity of the medium produced by irradiation and the direction of the radiation-chemical reactions involving the charged particles. In some cases it is important to be able to calculate the total yield of charged particles (called the initial ionisation yield).

In flash photolysis the energy of the electron produced by the ionisation process is not usually sufficient to cause further ionisation of a molecule of the matrix: often it cannot even excite the molecule to an excited state. In this case we are dealing with the generation of isolated ion pairs. An analogous situation exists under radiolysis, but only for the secondary δ-electrons, whose energy is less than a few eV. However, in contrast to the photolysis case, during radiolysis with γ-quanta or fast electrons of 1–10 MeV energy the fraction of the energy expended in forming isolated pairs is quite low (a figure of ~30% has been suggested[10-13]). About 40% of the energy is spent in the generation of "spurs", containing 2 or more pairs of charges (up to 10), and 10% in the formation of spherical, multiply-charged ionisation regions containing 10–50 ion pairs. Lastly, the remaining 20% of the energy is dissipated in forming short cylindrical tracks with an ionisation density approaching that of 1–2 MeV protons but less strong than that of α-particles ($E_\alpha = 3-5$ MeV). Of course, the tracks of the δ-electrons are very much shorter than those of heavy charged particles[14-18].

The Onsager and the Poole–Frenkel' theory are often used to calculate the yields of free charges from isolated pairs. The yield of charges from the tracks of heavy charged particles and from spurs can be described in terms of the theoretical concepts developed by Jaffe and Lea.

Whereas in the radiation chemistry of water and other polar liquids the real structure of the track of a fast electron is allowed for in the calculation of the yield of charges into the bulk of the liquid, in the radiation chemistry of non-polar solid or liquid organic systems (mostly, hydrocarbons) all the calculations so far have assumed radiolysis by the ion-pair mechanism. However, the need to allow for the contribution of formations with multiple charges to the observed radiolytic effect is being increasingly recognised[6,7,19-21].

1. Ion Pair Generation

a) Onsager's theory

Onsager[22,23] considered the probability of dissociation of a pair of charges in thermal equilibrium with a medium of temperature T and static dielectric constant $\varepsilon\varepsilon_0$ in an electric field E_0 for an initial separation of the pair of charges r_0. The subsequent motion of the charges was assumed to be determined by diffusion (diffusion coefficient $D = D_+ + D_-$) and drift in the combined field $E_0 + E_C$ (where E_C is the coulombic field due to two unlike charges having a mobility $\mu = \mu_+ + \mu_-$). To solve this problem Onsager used Smoluchowsky's equation and expressed its stationary solution as a power series.

The problem was subsequently discussed many times[6,7,24-46], and for an isotropic initial distribution of thermalised electrons the probability of dissociation of a bound pair in the weak field approximation was shown to be

$$\Phi(r_0, E_0) = \Phi(r_0)\left[1 + \frac{e^3}{8\pi\varepsilon\varepsilon_0 k^2 T^2} E_0\right], \qquad (1)$$

where e is the electronic charge, k is Boltzmann's constant, T is the absolute temperature (K), and $\Phi(r_0) = \exp(-r_C/r_0)$, where $r_C = e^2/4\pi\varepsilon\varepsilon_0 kT$ is the Onsager radius. The coefficient $\beta_0 = e^3/8\pi\varepsilon\varepsilon_0 k^2 T^2$ has been called the Onsager field constant. In the presence of strong electric fields this approximation is not valid, and $\Phi(r_0, E_0) \to 1$ when $E_0 \to \infty$.

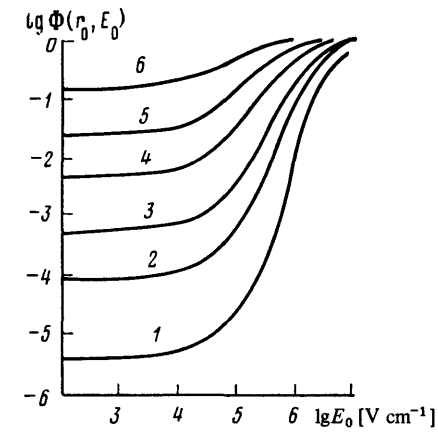


Figure 1. Dissociation probability Φ of a bound pair against E_0 for different initial distances: *1*) 1.5, *2*) 2.0, *3*) 2.5, *4*) 3.5, *5*) 5, *6*) 10 nm; $\varepsilon = 3.0$, $T = 300$ K[29].

For the typical values $\varepsilon = 3.0$ and $T = 300$ K the constants r_C and β_0 become 18.5 nm and 3.6×10^{-5} cm V^{-1} respectively. Numerical calculations of $\Phi(r_0, E_0)$ (Fig. 1) show a strong field and temperature dependence for small values of r_0 ($\lesssim 5.0$ nm).

If $g(r_0)$ is the probability density of the distribution of the bound pair with respect to initial separation ($\int_0^\infty g(r_0) 4\pi r_0^2 dr_0 = 1$) and G_0 is the initial ionisation yield it follows that the yield of free charges $G_{fi}(E_0)$ in the electric field E_0 can be expressed as

$$G_{fi}(E_0) = G_0 \int_0^\infty g(r_0)\,\Phi(r_0, E_0)\, 4\pi r_0^2 dr_0. \qquad (2)$$

Noting that $\Phi(r_0, E_0)$ in the weak field region is a linear function of E_0, and β_0 is independent of r_0, we can easily show that

$$G_{fi}(E_0) = G_{fi}(0)\,[1 + \beta_0 E_0], \qquad (3)$$

where $G_{fi}(0)$ is the yield of free charges in the absence of the electric field. Thus the dependence of G_{fi} on E_0 in the weak field region is linear, and therefore both $G_{fi}(0)$ and β_0 can be easily determined. This conclusion from the Onsager theory has been widely used as a test of the theory in concrete cases[47-49].

The above approach has proved very fruitful in explaining various phenomena observed in liquid-phase radiolysis, quantitative as well as qualitative agreement with experiment being obtained in many cases[6,7,50-53]. In the absence of a strict theory of the retardation and thermalisation of electrons in a condensed phase[54-62] the experimental dependence of the yield of free charges on the temperature T or on the field E_0 is often used to determine the form of the distribution function $g(r_0)$ (usually in the one-parameter approximation). The following distribution functions are most commonly used[30]:

1) the δ-distribution

$$g(r_0) = \delta(r_0 - R)/4\pi r_0^2;$$

2) the undistorted Gaussian distribution (UG)

$$g(r_0) = \pi^{-3/2} R^{-3} \cdot \exp(-r_0^2/R^2);$$

3) the distorted Gaussian distribution (DG)

$$g(r_0) = (4\pi^{3/2}\sigma R^2)^{-1} \cdot \exp(-(r_0 - R)^2/\sigma^2),$$

with the usual assumption that $\sigma = 0.25\ R$, and R is the mean thermalisation length of the electron;

4) the exponential distribution (ED)

$$g(r_0) = (4\pi R r_0^2)^{-1} \cdot \exp(-r_0/R).$$

Table 1. Values of the parameter R for different $g(r_0)$ distributions and other characteristics of organic liquids at ~296 K.[6,30]

Compound	R, nm				ε	r_c, nm	$G_{fi}(0)$	μ, cm² V⁻¹ s⁻¹	$10^6\beta_0$, V⁻¹ cm	
	δ	UG	DG	ER					calc	exper
n-Pentane	9.03	7.13	8.28	6.23	1.842	30.6	0.14	0.16	6.00	—
Isopentane	9.50	7.58	8.70	6.76	1.84	30.6	0.17	—	—	—
Neopentane	19.71	17.82*	18.32	21.20	1.77	31.7	0.86	35.0	6.22	6.04
Cyclopentane	8.66	6.90	7.96	6.08	1.960	28.8	0.15	—	5.65	—
3-Methylpentane	8.78	6.95	8.08	6.06	1.901	29.65	0.15	—	5.81	—
n-Hexane	8.57	6.76	7.85	5.79	1.885	29.9	0.13	0.1	5.36	5.81
									10.7**	11.2**
Cyclohexane	8.28	6.56	7.60	5.75	2.022	27.9	0.15	0.35	5.47	—

* By applying a correction to Onsager's theory for the dependence of the mobility μ on the electric field E_0 (assuming $E_0 \geq E_{cr}$) Mozumder obtained[63] an R value of 7.7 nm for neopentane. This result is obviously controversial.
** At 219 K.

Numerical values of the parameters used to determine the yield of charges in various organic liquids at room temperature ($T = 296$ K) are given in Table 1. We note that the parameter R is much higher in neopentane than in n-hexane. Direct measurements[59] of the relaxation length (i.e. the distance over which the flow of photo-generated electrons decays by a factor of e) in films of these two compounds at low temperatures gave l_{rel} values of 3.0 and 15.7 nm respectively. Thus we can assume that the mobility of electrons is much greater in neopentane than in n-hexane.

In addition to describing accurately the stationary radiolysis ($t \to \infty$) results, Onsager's theory correctly interprets the kinetics of the process, and also the concentration dependence of the electron trapping processes[6,7]. Mozumder[64], using the prescribed diffusion method, obtained the following expression for the probability $F(t)$ which determines the relative number of bound pairs whose lifetime (before recombination) is $\geq t$:

$$F(t) = \exp\left\{-\frac{r_c}{r_0}\left[1 - \operatorname{erf}\frac{r_0}{(4Dt)^{1/2}}\right]\right\}. \quad (4)$$

As expected, $F(0) = 1$ and $F(\infty) = \exp(-r_c/r_0) = \Phi(r_0)$. Other approximate methods of calculating $F(t)$ are known[6,37,38]. A very simple method of estimating the recombination time of bound charges in a pair is an extension of the Stokes–Einstein relation to the case of the coulombic field of an ion, assuming that the terminal velocity is reached instantaneously[65]. This method leads to the "r_0^3" formula

$$t_{rec} = \frac{4\pi}{3}\frac{\varepsilon\varepsilon_0 r_0^3}{e\mu}.$$

For the distance $r_0 = r_c$ we obtain $t_{rec}^{max} = r_c^2/3D$.

A numerical solution of the non-stationary Smoluchowski equation is given in Ref.66 for a model dielectric having the parameters $D = 9.27 \times 10^{-3}$ cm² s⁻¹, $\varepsilon = 2.023$, $r_c = 27.9$ nm, and $r_0 = 8.0$ nm. It is shown† that $t_{1/2} \cong 10^{-11}$ s irrespective of E_0 (as long as $E_0 \leq 10^5$ V cm⁻¹). The field E_0 begins to influence the recombination kinetics of the charges when $t \geq 2 \times 10^{-11}$ s.

The Laplace transform has been used[67,68] to establish the relationship between the concentration dependence of the trapping probability $F(c)$ and the probability density of the lifetime of the bound pairs $dF(t)/dt$, and experimental data on electron trapping in non-polar liquids have been fully analysed[69,70]. Since

$$1 - f(c) = \int_0^\infty \frac{dF(t)}{dt}\exp(-kct)\,dt \quad (5)$$

(where k is the rate constant of the reaction between an electron and the acceptor, and c is the concentration of the acceptor, $f(c) = (\alpha c)^{1/2}/[1 + (\alpha c)^{1/2}]$, and α is a constant), we can apply the inverse Laplace transform and obtain

$$dF(t)/dt = \lambda[(\pi\lambda t)^{-1/2} - \exp(\lambda t)\operatorname{erfc}(\lambda t)^{1/2}]. \quad (6)$$

In this expression $\lambda = k/\alpha$, and $\operatorname{erfc}(x) = 1 - \operatorname{erf}(x)$. Hence we arrive at

$$F(t) = \exp(\lambda t)\operatorname{erfc}(\lambda t)^{1/2},$$
$$F(t) \approx (\pi\lambda t)^{-1/2} \quad \text{for} \quad \lambda t \geq 100. \quad (7)$$

Thus the initial decrease in the number of bound pairs in a non-polar liquid is very fast (with a half-life $t_{1/2}$ defined by the expression $\lambda t_{1/2} \cong 0.59$), but this is followed by a slower decay. According to Zador and coworkers[71] $t_{1/2} = 0.6 \times 10^{-12}$ s for cyclohexane at room temperature ($\lambda = 0.9 \times 10^{12}$ s⁻¹), but a later paper from the same laboratory[72] gives $t_{1/2} \cong 1.3 \times 10^{-12}$ s. At time $t = 10^{-8}$ s only 0.6% of the original number of bound pairs is still present ($G_0 = 4.0$), which is less by a factor of ~5 than the number of free charges in the liquid ($G_{fi}(0) \cong 0.12$).

In the general case we have, for non-polar liquids,

$$G(t) = G_{fi}(0) + [G_0 - G_{fi}(0)] \cdot F(t). \quad (8)$$

Several workers[73–75] have used the r_0^3 formula to calculate the distribution function $F(t)$ in liquid hydrocarbons, as well as the exponential form of the probability density distribution $g(r_0)$[73] or a similar expression[74]. It was shown that $t_{1/2}$ for n-hexane at room temperature is 3.5×10^{-12} s with $G_0 = 4.0$. On lowering the temperature $t_{1/2}$ is found to increase, reaching 0.13×10^{-9} s at −80 °C. The authors[74] point out that the expected diffusion-determined relationship $F(t) \propto t^{-1/2}$ at $t \to \infty$ is not obeyed; this is a consequence of using the r_0^3 formula, which ignores diffusion. However, at large values of r_0 (approaching r_c) the importance of diffusion increases, while the role of drift in the coulombic field of the ion becomes less important.

An analysis[76] of the validity of the Laplace transform for real liquids, in which the mobility is determined by trapping processes, suggests that Eqn.(5) is not applicable in general. However, the asymptotic behaviour of $F(t)$ at $t \to \infty$ or of $f(c)$ at $c \to 0$ is unchanged. We should also mention a series of papers[77–79] in which Onsager's theory is used to calculate the field dependence of the quantum yield of hot electrons injected into a dielectric by a metallic electrode. In the one-dimensional problem (but not in the three-dimensional problem) it is found that $G_{fi}(0) = 0$.

† $t_{1/2}$ is the time in which $F(t)$ decreases by a factor of 2 from 1.0 to 0.5.

The Poole–Frenkel' theory

The classical Poole–Frenkel' effect refers to the non-linear increase in electrical conductivity in strong electric fields (in the dark). One possible explanation of this effect relies on the lowering of the energy barrier opposing the ionisation of the neutral donor in the direction of the applied field E_0 by an amount $\Delta W = \beta E_0^{1/2}$, where $\beta = (e^3/\pi\varepsilon\varepsilon_0)^{1/2}$ is the Poole–Frenkel' constant. In this case the probability of thermal ionisation of the neutral donor in the field E_0 increases by a factor of $\exp(\beta E_0^{1/2}/kT)$. This simple model has been used to explain the non-linear behaviour of the photo-current in strong fields[80,81]. By allowing for the recombination of the pairs Tabak and Warter[81] obtained an approximate expression for the quantum yield of free charges:

$$\eta = \left[1 + (\nu t_{rec})^{-1} \exp\left(\frac{E_a - \beta E_0^{1/2}}{kT}\right)\right]^{-1}, \quad (9)$$

where ν is the frequency factor, E_a is the activation energy (height of the potential barrier), and t_{rec} is the mean recombination time.

The model has been developed further[82,83] (see also Refs. 31, 47, 84, 85). The thermalisation length of the electron has been calculated by the diffusion approximation (equating the rate of energy loss to $h\nu_p^2$, where ν_p is the phonon frequency and h is Planck's constant), so that $r_0 = (Dt)^{1/2}$. Allowing for the energy of the coulombic and of the externally applied field changes the form of Eqn.(9), since

$$E_a = e^2/4\pi\varepsilon\varepsilon_0 r_0 + eE_0 r_0;$$

and r_0 is given by the expression

$$\frac{h\nu_p^2}{D} r_0^2 = (\hbar\omega - E_g) + \frac{e^2}{4\pi\,\varepsilon\varepsilon_0 r_0} + eE_0 r_0,$$

where E_g is the width of the forbidden gap of the dielectric. With these corrections the expression for η gives a qualitatively correct description of the dependence of the photo-ionisation quantum yield on the photon energy ($\hbar\omega$) and on the strength of the externally applied field. However, a quantitative comparison of theory and experiment is complicated by the large number of undetermined parameters (t_{rec}, ν_p, ν) which cannot be obtained directly from experimental results.

In some recent publications the descriptions of the photolysis of various substances by the Onsager and the Poole–Frenkel' theory are compared[31–33,86–97]. In every case the Onsager theory is preferred. However, it has been pointed out[91,95] that both the Onsager and the Poole–Frenkel' mechanism may be operative in most cases. Depending on the value of r_0, and hence of the mean free path λ, either of these mechanisms could be predominant. When r_0 is much smaller than λ (and the diffusion of the electron within the Onsager sphere plays the major role) the yield of free charges from the bound pairs is directly described (for both radiolysis and photolysis) by the Onsager theory. On the other hand if r_0 is large (and of the same order as r_c) the decrease in height of the coulombic potential barrier under the influence of the external field (Poole–Frenkel' mechanism) becomes predominant. Furthermore, in the case of photo-excitation we should allow for surface recombination[89,92,93], which can cause large discrepancies in the yield of free charges at low field strengths from the values predicted by Onsager's theory[89].

2. Tracks and Multiply Charged Spherical Formations

Classical calculations of the yield of charges in the volume from tracks and from multiply charged spherical formations have been published by Jaffe and Lea[98–100] (see also the review articles in Refs.6, 7, and 19). In these calculations ions of opposite signs are assumed to be distributed in equal concentrations according to a Gaussian law with respect to the axis of the track or to the centre of the agglomerate (depending on the type of geometry). It is also assumed that the distribution curve remains Gaussian, but the width of the distribution changes with time as $r(t) = (b^2 + 4Dt)^{1/2}$, where b is the initial radius of the track (at the instant of formation). With these assumptions the authors calculate the decrease in the total number of charges as a function of time, which in the limit of $t \to \infty$ gives the relative number of charges reaching the volume of the sample. No allowance is made for polarisation by the external electric field. When the track is perpendicular ($\perp$) to the field E_0, and $t \to \infty$, the yield of charges from the tracks into the volume is given by

$$f_{tr}^{\perp} = \left[1 + \frac{k_r N_0}{8\pi D} (\pi/z)^{1/2} S(z)\right]^{-1}, \quad (10)$$

where

$$z = b^2\mu^2 E_0^2/2D^2, \text{ and } S(z) = \frac{1}{\pi^{-1/2}} \int_0^{\infty} \frac{\exp(-s)\,ds}{[s(1 + s/z)]^{1/2}};$$

$k_r = (e/\varepsilon\varepsilon_0)\mu$ is the recombination coefficient, and N_0 is the initial linear ionisation density in the case of the track.

Values of the function $(\pi/z)^{1/2}S(z)$ are given in graphical form in Refs.101–103. In the case of a short cylindrical track, with $N_0 = 5 \times 10^7$ cm^{-1} ($b = 10^{-6}$ cm) and $\mu = 10^{-5}$ cm^2 V^{-1} s^{-1} (say), we find that for E_0 values of 0, 10^2, 10^3, 10^4, 10^5, and 10^6 V cm^{-1} the $f_{tr}^{\perp}$ values are 0, 10^{-3}, 1.6×10^{-3}, 3.7×10^{-3}, 2.1×10^{-2}, and 19.4×10^{-2} respectively. For $r_0 =$ 5.0 nm we have $\Phi(r_0, E_0) \geq f_{tr}^{\perp}(E_0)$, the difference being largest in weak electric fields# ($E_0 \leq 10^4$ V cm^{-1}).

By using the prescribed diffusion method Mozumder[105,106] showed that Eqn.(10) is valid even on the assumption that the positive ions are distributed only along the axis of the track. He also showed that the rates of recombination of the charges in short tracks and spurs containing 10 pairs of charges are approximately equal, and that in a medium in which the diffusion coefficient of trapped electrons is $\sim 2 \times 10^{-3}$ cm^2 s^{-1} (i.e. $\mu_{dr} = 10^{-1}$ cm^2 V^{-1} s^{-1} at 300 K) the half-life $t_{1/2}$ is $\sim 3 \times 10^{-12}$ s (assuming an initial charge density in the tracks and spurs of $\sim 5 \times 10^{18}$ cm^{-3}). The yield of charges into the volume after irradiation with α-particles having energies of several MeV has been shown[107] to be ~ 10 times lower than after irradiation with fast electrons or γ-rays: this is because the N_0 parameter for δ-electrons of 1.0–5.0 keV energy is ~ 10 times lower than for the tracks of α-particles[19].

III. PROCESSES INVOLVING THE MOTION OF CHARGES UNDER THE INFLUENCE OF AN EXTERNAL(OR INTERNAL) ELECTRIC FIELD

As stated above, ionisation during radiolysis or photolysis is accompanied by the appearance of non-equilibrium (excess) charges whose motion in an external field is responsible for the induced conductivity. Extensive experimental investigations have shown that, in addition to the normal charge

The estimated values of $f_{tr}^{\perp}$ are probably much too high because no allowance was made for the polarisation of the track[104].

transfer and recombination processes, charge trapping can occur on relatively deep traps of physical or chemical origin. The trapped (stabilised) charges can persist for very long times, especially at low temperatures, thus giving rise to a whole series of new properties in the irradiated material (photo-stimulated conduction (PSC) in the visible and i.r. regions, thermally stimulated currents (TSC) when the sample is allowed to warm up, a sharp increase in recombination luminescence under i.r. illumination or on applying a strong electric field—the electro-photoluminescence phenomenon or Gudden–Pohl effect). The intensity of all these processes decreases with time to the initial values, characteristic of the non-irradiated materials. Therefore re-irradiation of the material is required each time one of these effects is to be observed.

1. Radiation-Induced Electrical Conductance

Measurements of electrical conductivity are one of the most direct methods of observing the charged particles during the early (physicochemical) stage of the radiolysis[108,109] §. In principle the method allows the properties of a quasi-free ("dry") electron to be studied before its solvation or capture by the medium. However, at the moment the time resolution of this method is greatly inferior to that of the optical method of detecting short-lived particles (0.2×10^{-9} s and 10^{-12} s respectively)[110–112].

Measurements of the radiation-induced electrical conductivity of polymeric dielectrics, using both pulsed and continuous radiation, are reported in Refs. 19, 102, and 113.

According to modern ideas, the instantaneous component (rise and fall time ≤ 1 ns) of the radiation pulse electrical conductance (RPEC) in disordered solid systems is associated with the quasi-free state of the electron, characterised by a microscopic mobility μ_0 (1–100 $cm^2\ V^{-1}\ s^{-1}$). This interpretation is confirmed by the observation that the proportionality coefficient K_{inst} between the volume conductivity (γ_{inst}) and the dose of radiation absorbed (P) is independent of the intensity of the applied electrical field E_0 ($\leq 5 \times 10^5$ V cm^{-1}), and is only weakly dependent on temperature[19,102].

Table 2. Values of K_{inst} ($ohm^{-1}\ cm^{-1}\ Rad^{-1}\ s$) for some polymeric materials[114–120].

Material	$10^{19}K_{inst}$	ε (Ref. 121)
Poly(tetrafluoroethylene) (PTFE)	31	2.0
Low-pressure polyethylene (LPPE)	11	2.2–2.4
High-pressure polyethylene (HPPE)	3.0	
Polypropylene	3.0	2.15–2.35
Poly(ethylene terephthalate) (PETP)	2.0	3.10–3.40
Polystyrene	1.4	2.6
PM-1 polyimide	1.2	4.0
Crystalline poly(chlorotrifluoroethylene) (F-3)	0.4	3.0
Poly(vinylidene fluoride) (F-3)	0.20	3.0
Poly(vinylidene fluoride) (F-2)	0.18	9.5
Poly(vinylidene chloride)	0.20	2.85
Poly(vinyl chloride) (PVC)	0.12	3.05
Poly(methyl methacrylate) (PMMA)	0.16	3.20

The K_{inst} values for a number of polymeric materials at room temperature are given in Table 2. We note that the K_{inst} values for non-polar polymers are higher than those for polar polymers (for example, two orders of magnitude higher for PTFE than for PMMA). Furthermore, an increase in the degree of crystallinity of a given material produces a slight increase (approximately 2-fold) in K_{inst}.[114,120]

The parameter K_{inst} is defined by the equation

$$G\mu_0\tau_s(cm^2\ V^{-1}) = \frac{10^7}{\rho}K_{inst}(ohm^{-1}\ cm^{-1}\ Rad^{-1}\ s), \qquad (11)$$

where τ_s is the life time of the quasi-free electron, and ρ is the density of the dielectric (g cm^{-3}). Taking $G = 1.0$ (for $E_0 = 5 \times 10^5$ V cm^{-1}) and $\mu_0 = 10\ cm^2\ V^{-1}\ s^{-1}$ we find that $\tau_s = 2 \times 10^{-13}$ s for PTFE (and an even smaller value for PMMA). This estimate confirms that the lifetime of the quasi-free charge carriers is comparable with the thermalisation time (10^{-13}–10^{-14} s). It has even been suggested[120,122–127] that the life time could be shorter than the thermalisation time.

The experimentally observed lack of dependence of K_{inst} on the dose per pulse (in the range 1–10^6 Rad)[128] suggests a very high concentration of electron (or hole) traps (10^{18}–10^{21} cm^{-3}). Somewhat different results were obtained by Hughes[129–132] after a study of the RPEC of amorphous (fused) SiO_2 (quartz). By using very pure amorphous SiO_2 he was able to determine μ_0, τ_s, and G_0 independently (20 $cm^2\ V^{-1}\ s^{-1}$, 14 ns, and 3.6 respectively). The dependence of G on E_0 predicted by Onsager's theory was observed for $r_0 = 10.0$ nm.

In contrast to pulse irradiation, for which K_{inst} is independent of E_0 ($< 5 \times 10^5$ V cm^{-1})[117–119], in the case of continuous irradiation the electrical conductivity increases with E_0[133] as predicted by the Onsager theory.

Systematic studies of the relaxation of RPEC in polymers and in ceramic materials[116,134,135] have confirmed previous reports of the independence of the kinetics on the dose of radiation. Thus, changes in the dose per pulse of more than three orders of magnitude had no effect on $\tau_{1/2}$ for PTFE and the UF-46 ceramic[134,135]. Similarly, in the case of polystyrene an increase in the dose from 1 to 4×10^6 Rad (Refs. 136 and 137 respectively) caused an increase in $\tau_{1/2}$ from 3 to 8 μs, probably due to the change in pulse length from 0.1 to 4.0 μs.

These results suggest that the recombination of charge carriers is inhomogeneous at short irradiation times. This conclusion is confirmed by the kinetics of photocurrent decay in hydrocarbons previously subjected to radiolysis at 77 K.[138]

Explanations of two types have been proposed for these features of the process (the dose-independent, hyperbolic decay of the RPEC, and the lack of dependence of K_{inst} on E_0). In the first approach the inhomogeneity of the recombination kinetics is ascribed to the neutralisation of charged particles in isolated bound pairs, and the induced electrical conductivity to the motion of electrons under the influence of the external field and of the coulombic field of the parent ion (E_C).[138–146] This model also explains the decay kinetics of the i.r.-stimulated current in frozen and irradiated hydrocarbons. The conditions for the validity of this model are defined by the inequalities $\mu_0\tau_s \leq 10^{-10}\ cm^2\ V^{-1}$ and $G_g \geq G_{fl}$ (where G_g is the yield of bound charges).

Of course, electric currents involving these non-dissociated pairs are self-polarising. Unlike the classical types of dielectric polarisation (electronic, ionic, and Maxwell–Wagner polarisation) this polarisation should produce (after the irradiation) negative currents in spite of the presence of an external field[127]. However, the present writers doubt whether negative currents can ever be observed in real systems because of the slowness of the pair recombination process.

§ See also the recently published monograph: A.K.Pikaev, S.A.Kabakchi, I.E.Makarov, and B.G.Ershov, "Impul'snyi Radioliz i Ego Primenenie" (Pulse Radiolysis and Its Applications), Atomizdat, Moscow, 1980, p. 279.

The second approach[104,116,134,135] relates the inhomogeneity of the RPEC decay kinetics to the recombination of charge carriers in track-like formations (mainly, in short cylindrical tracks), and it assumes that the contribution from electrons in bound pairs to the electric current is much smaller than that of free electrons, so that the recombination kinetics of charges in the pairs are not reflected in the decay of the radiation-induced current. The yield of charges able to contribute to the electric current is determined not only by the yield of free charges from bound pairs as a result of thermal dissociation and separation in an electric field (as in Onsager's theory), but also by the total yield of charges in the short tracks. The ratio of the yields of triplets and singlets in the irradiation of tetracene by α-particles was found to be 3 : 1, which is characteristic of the recombination of random partners[147,148]. This means that no correlation exists within the tracks between the electron and the parent ion, i.e. the track can be treated as a dense solid-state plasma region. The polarisation of the track in an electric field by the motion of its constituent charges is of the classical Maxwell–Wagner type, and should not cause the appearance of negative currents after completion of the irradiation in the presence of the electric field E_0.

However, a consequence of this model is that in strong electric fields ($\sim 10^6$ V cm^{-1}) the yield of free charges from isolated pairs may be greater than the yield of charges in the short cylindrical tracks. Thus we would expect an increase in K_{inst} in very strong fields[117]. Furthermore, the model can be used to calculate (using experimental data on the delayed component of the RPEC) the initial density of charges in the short cylindrical track and μ_{dr}. In the case of polyimides these two parameters were found[118] to be 4.5×10^{18} cm^{-3} and 3.6×10^{-7} cm^2 V^{-1} s^{-1} (for $E_0 = 10^6$ V cm^{-1}), in good agreement with published data[149,150].

2. Recombination Luminescence

Recombination luminescence (RL) is one of the most fully investigated effects accompanying the radiolysis or photolysis of solid organic systems. A detailed discussion of the results obtained up to 1970 can be found in a number of monographs and review[1-3,151,152]; more recent results have also been included in review articles[153-158].

The emission of light has been shown to be a direct consequence of the evolution of energy attending the recombination of opposite charges (whether free, or bound), the intensity of the luminescence being proportional to the rate of disappearance of charges through recombination[159-161]. (Some anomalies in this proportionality are considered in Ref.156.) Although the quantum yield of RL is usually small, the method is extremely sensitive ($\sim 10^7$ quanta, as compared to 10^{11}–10^{13} spins in the ESR method and 10^{15}–10^{16} molecules in the absorption spectroscopy method), and therefore it has been widely used to study charges stabilised in a condensed phase. The following are the main areas of research in which the method has been most successfully applied: 1) studies of charge recombination mechanisms, and estimates of the relative contributions of diffusional and tunnelling transport to the process; 2) influence of the nature of the medium on the ionisation potential of an impurity; 3) studies of the mechanism of elementary reactions leading to the emission of light quanta; 4) studies of the effect of various external factors (temperature, electric field, illumination) on the recombination process.

The diffusion approach to the calculation of the decay kinetics of isothermal recombination luminescence (IRL) during photo-ionisation of aromatic amines in polar solvents (water, methanol, glycerol, or their mixtures) at 77 K was used in Ref.162 without allowance for the effect of the coulombic field of the parent ion on the diffusional motion of the electron. By selecting a suitable initial distribution of the electrons in pairs with respect to the distance (r_0) from their corresponding ion a relationship similar to that observed experimentally was calculated between the IRL intensity (L_{IRL}) and the time elapsed after the end of the u.v. irradiation:

$$L_{IRL} = Kt^{-m}, \tag{12}$$

where K and m are constants, with $m \cong 1.0$.

Subsequently the diffusion model (modified by the inclusion of a term for the coulombic interaction between charged particles) was used successfully to explain a wide range of phenomena.

Abell and Mozumder[163] concluded from an exact solution of the Smoluchowski equation that Eqn.(12) can be applied only over a narrow range of t values (no more than 1.5–2 orders of magnitude), whatever the initial distribution $g(r_0)$ of the electrons in the pairs: this conclusion differs from that of Debye and Edwards[162], who did not impose any limits on their range of t. The expression for L_{IRL} becomes

$$L_{IRL} \propto t^{-3/2}, \tag{13}$$

which follows directly from Eqn.(7). Under these conditions the diffusional recombination process should be activation-limited, and therefore strongly temperature-dependent. However, neither of these predictions of the diffusion theory is fulfilled in practice. The IRL decay kinetics are independent of temperature over times between 10^{-6} and 10^3 s[164,165]: the decay curve is accurately described by the expression

$$L_{IRL}(0)/L_{IRL}(t) = 1 + K_1(t-t_0). \tag{14}$$

Similar results have been obtained by other workers[166-181]. The hypothesis that charge recombination (especially at low temperatures) is the result of a tunnelling transition of the electron from the anion to the cation has been put forward increasingly in recent years. It is suggested[182] that the tunnel effect can extend over relatively large distances (up to 50 Å), by analogy with the recombination of an F-centre electron in alkali halide crystals[183]. Approximate theories of this phenomenon have been proposed by many workers[184-206].

It has been shown[207-209] that the presence of a slight activation energy ($E_a \cong 0.02$ eV) is not inconsistent with a predominantly tunnelling transfer mechanism, since the many possible equilibrium configurations of a trapped electron in frozen organic systems probably have a finite spread in energy.

By assuming an exponential distribution function $g(r_0)$ (see Section I) the following expression for L_{IRL} has been obtained[187,189]:

$$L_{IRL} = \alpha\nu \frac{a}{b} \Gamma\left(1 + \frac{a}{b}\right) N_0 (\nu t)^{-(1+a/b)}, \quad \nu t \gg 1, \tag{15}$$

where a is the damping parameter of the wave function, b is the parameter of the distribution function $g(r_0)$, ν is the frequency factor, N_0 is the initial concentration of isolated pairs, α is a constant, and $\Gamma(x)$ is the gamma-function. Since $a \ll b$ Eqn.(15) reduces to (12) for $m = 1.02$. The frequency factor is very large, and therefore the condition $\nu t \gg 1$ is always satisfied. The time dependence of $g(r_0, t)$ is illustrated in Fig.2.

It is thought[184] that the tunnel mechanism of recombination can explain the very low limiting concentrations of ions which are stabilised during low-temperature radiolysis (10^{17}–10^{18} cm^{-3}, which is only a small fraction of the total number of traps[1,143]). The limiting concentrations of free radicals for

similar doses of radiation are substantially higher (10^{19}–10^{20} cm^{-3}).

The tunnelling hypothesis has allowed satisfactory explanations to be proposed for a number of experimentally observed features of electron trapping in frozen matrices which could not be explained by the classical diffusion theory[171,186,195,200,202,210–213].

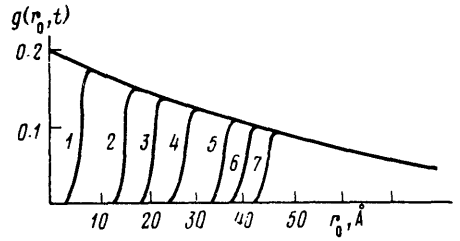


Figure 2. Plots of $g(r_0,t)$ for different times (*1*) 1 ps, *2*) 1 ns, *3*) 1 μs, *4*) 1 ms, *5*) 1 s, *6*) 1 min, *7*) 1 h) in the tunnelling mechanism for the recombination of bound pairs during low-temperature radiolysis or photolysis; $\nu = 10^{15}$ s^{-1}, $a = 1$ Å, $b = 50$ Å.[189]

It was established that the decay kinetics of L_{IRL} are relatively insensitive to the type of radiation (photolysis, or radiolysis)[214,215]. In photolysis studies a more uniform ionisation density over the thickness of the initial matrix is often achieved by using additives[152,156,216] requiring two quanta for ionisation of the molecule. The commonest of these additives are *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) and tryptophan. The physical characteristics of the TMPD–methylpentane (3-MP) solid solutions which have been used[217–222] at 77 K are summarised below:

Parameter	Value
Concentration range of TMPD in 3-MP	(1.0–3.0) × 10^{-3} M; (0.6–2.0) × 10^{18} cm^{-3}
Density	0.88 g cm^{-3}
Viscosity	10^{12} Pa s
Glass formation temperature	77 K
Static dielectric constant	2.3
Onsager radius r_c	95 nm
Field constant β_0	5.7 × 10^{-4} cm V^{-1}
Red absorption edge TMPD	360 nm (3.44 eV)
Ionisation potential of TMPD in the gas phase	6.7 eV
Ionisation potential of TMPD in the solid solution	5.9 eV
Lifetime of the triplet state	2.3 ± 0.3 s

As we have already pointed out, the photo-ionisation of the TMPD molecules takes place in two steps: initially the molecule is excited into a singlet state ($\lambda \leq 360$ nm), from which it passes into the triplet state by intersystem crossing, and the absorption of a second light quantum ($\lambda \leq 400$ nm) in the triplet state causes ionisation of the molecule. Two-quantum ionisation of commercial polyethylene under u.v. irradiation has been reported also in Ref. 223.

Characteristic decay curves of L_{IRL} of a TMPD–3-MP solid solution after u.v. irradiation ($\lambda = 313$ nm) for different times (τ_1, $2\tau_1$, $20\tau_1$) are shown in Fig. 3. On the linear portion of the plot of L_{IRL} against exposure time τ the slope is proportional to the square of the intensity of u.v. radiation, as expected for a two-quantum ionisation process. For $\tau \leq 2\tau_1$ (≤ 30 s) the charges are generated mainly as bound pairs, and the yield of free charges is very small. In this range of exposures the TMPD–3-MP solution displays electrophotoluminescence (EPL)[224,225]: the application of a strong electric field ($> 2.2 \times 10^5$ V cm^{-1}) produces a flash of recombination radiation, and a second application of a field of equal strength but opposite polarity produces another flash. Further observation of the effect is possible only if the sample is irradiated again. The amplitude of the RPL flash is exponentially dependent on the strength of the electric field:

$$L_{EPL}(0) = A \exp(\alpha E_0/kT), \qquad (16)$$

where $\alpha \approx 0.9$–1.7 Å. (An explanation of the EPL phenomenon with allowance for electron tunnelling is given in Refs. 196 and 226–230.)

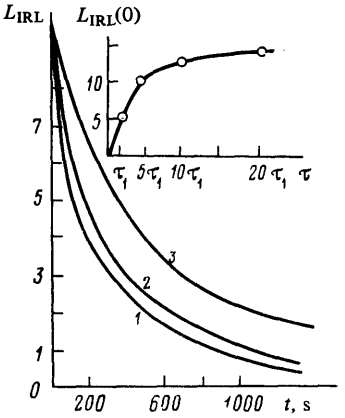


Figure 3. Intensity of isothermal recombination luminescence (L_{IRL}) against time; $\tau_1 = 15$ s, $T = 77$ K[152]; $\tau = \tau_1$ (*1*), $\tau = 2\tau_1$ (*2*), and $\tau = 20\tau_1$ (*3*).

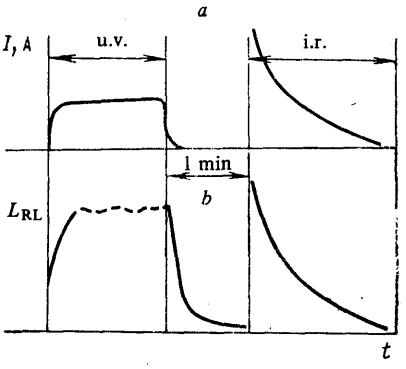


Figure 4. Comparison of the kinetics of photo-stimulated conduction (*a*) and recombination luminescence (*b*) in TMPD–3-MP at 77 K; $\lambda_{u.v.} = 313$ nm, $\lambda_{i.r.} = 694$ nm.[234]

By using a distorted Gaussian distribution centred on $\bar{r}_0 = 32$ Å, with a dispersion parameter of 6.2 Å and a life time for a trapped electron of 10^3 s, the kinetics of the decay in frozen TMPD–3-MP solutions have been described quantitatively[231–233] to an accuracy of 3%. It has been suggested that the lifetime of the trapped electrons decreases exponentially as the strength of the external field increases, thus increasing the probability of a tunnelling transition to the parent ion[196].

Experimental results reported in Refs. 221 and 234 (Fig. 4) give additional information on the possible contribution from electrons in bound pairs to the observed electric current. It has been established that during i.r. irradiation ($\lambda = 694$ nm) only ~50% of the bound pairs initially formed by u.v. irradiation are able to recombine (higher-energy radiation is needed to cause annealing of the remaining pairs). Since at 77 K the number of bound charges is much greater than the number of free charges, the photo-current produced by u.v. irradiation should be due to the polarisation of the bound pairs in the external electric field E_0 ($\ll E_C$).[139] However, in that case the net charge flowing in the external circuit as a result of the current stimulated by i.r. radiation should be negative, since the current is produced by the depolarisation of the bound pairs and is equal to one-half of the charge flowing through the external circuit in the case of u.v. illumination. Furthermore, the kinetics of the negative current (Fig. 4a) should be similar to the kinetics of the photo-stimulated IRL (Fig. 4b), as is found experimentally. However, the sign of the photocurrent observed in practice is the opposite to that predicted by the theory. It is also found that the recombination time of a bound isolated pair after the trapped electron has been set free by i.r. light is not greater than ~1 ns.[235]

On the assumption that only free charges can contribute to the photocurrent under u.v. irradiation[152,234], and noting that the lifetime of these charges before capture by a trap is less than 1 μs,[221] we can resolve the above inconsistency. By the same argument we can explain also the experimental finding[140] that i.r. irradiation of 3-MP previously exposed to low-temperature (77 K) radiolysis in the presence of an external electric field E_0 causes a negative current to flow when $E_0 = 0$. Thus, the appearance of a negative current can be ascribed to depolarisation of the short tracks (see Section II and Ref. 127).

As we have already pointed out, under u.v. irradiation the formation of free charges giving rise to the observed photocurrent is due to the ionisation (with a very low probability) of excited triplet molecules of TMPD, and in the case of i.r. irradiation it is due to optical ionisation of stabilised bound pairs (again, with a very low probability). In order to describe the experimental results quantitatively as well as qualitatively (Fig. 4) we have to postulate a relatively high drift mobility for the free electron formed as a result of u.v. or i.r. irradiation (a low-energy electron with energy ≤1 eV).

It is found[236] that the type of radiation used (light, or X-rays) has no effect on the decay kinetics of the recombination-induced phosphorescence of tryptophan in a frozen mixture of water and ethylene glycol, or on the thermo-luminescence curve. Similar results have been reported for less polar matrices[214,215,237]. However, there are regions of high local concentration of charge[236,239] produced by electron irradiation of the material: in strongly polar matrices these regions begin to disappear[240] only at times $>10^{-9}$ s. The need to allow for these effects in studies of the kinetics of IRL is stressed.

Recently published work[241] shows that the recombination probability of charges produced by u.v. irradiation is higher (by approximately 2) than when γ-radiation is used, at least in the case of a frozen solution of tryptophan in a mixture of ethylene glycol and water. It is also reported that the type of radiation (α or β radiation) can affect the decay kinetics of L_{IRL} in methylcyclohexane at 77 K, so that Eqn. (14) does not apply[242] at times between 1 and 500 ns (see also Refs. 243–245).

Neither the type of emitting centre nor the nature of the luminescence is yet fully understood. It is usually assumed that the recombination (followed by light emission) involves the scheme

$$A^+ + B^- \rightarrow A^* + B,$$
$$A^* \rightarrow A + h\nu, \qquad (17)$$

where B^- could be a trapped electron or an anion, and A is a molecule of solvent, solute, or radiolysis product. In some polymeric materials (polyethylene, polystyrene, PTFE, polypropylene) the luminescence centres can be carbonyl groups attached to the ends of molecular main chains or side chains[167]. However, the energy set free by the recombination process can be transferred to the impurity acting as a recombination centre[219,246]. It has been suggested[166,201] that radiative recombination by the scheme

$$A^+ + B^- \rightarrow A + B + h\nu, \qquad (18)$$

can explain the RL in pure alkenes during radiolysis. According to this mechanism photon emission and recombination occur simultaneously. The excited state of the luminescence centre is assumed to be formed by transfer of the recombination energy of the charges in the initial matrix[247–256].

Studies of the recombination-induced emission generated by the scheme (17) have shown that both fluorescence and phosphorescence of the molecule A can occur in non-polar matrices[165,170,219], but in strongly polar solvents only phosphorescence is possible[170] (see also Refs. 257 and 258).

Photo-excitation may occur through the ejection of a bound electron from a trap, and its recombination, or by a tunnelling transition of the electron from the excited state in the trap[177] at longer wave lengths ($\lambda > 900$ nm). In the former case we can expect both the triplet and the singlet level of the molecule A to be excited, whereas in the latter case the triplet state is preferentially excited. A study[160] of the effect of short illumination periods ($\lambda > 450$ nm), repeated at 20 s intervals, on the IRL curve of polybutadiene failed to detect a significant change in the population of the traps responsible for the isothermal decay of L_{IRL} at 90 K. However, a longer period of illumination (~7 min) can markedly increase the RL intensity observed as the sample is allowed to warm up to room temperature (especially at low temperatures). These experiments have confirmed the hypothesis that traps are present in large numbers, and with a depth distribution. Other workers came to a similar conclusion[223].

When a sample exposed to low-temperature hydrolysis is allowed to warm up the $L_{IRL} = f(T)$ curve contains several peaks whose position on the temperature scale can be correlated with the type of molecular motion which becomes "unfrozen" in this temperature range[256,259,260] or with structural changes associated with that motion[261–267]. The correlation can be explained by assuming a proportionality between the probability of setting the charge carriers free from their traps and the frequency factor of the appropriate molecular motion (note that thermal emission from a trap is accompanied by partial or total collapse of the trap as a result of the structural changes involved). An alternative explanation is possible: the softening of the matrix associated with the temperature rise allows faster diffusion of the trap (containing a captured electron) in the field of the cation. A 10 Å change in the distance between the two species is equivalent to an increase of 10^4–10^5 times in the probability of electron tunnelling[175], which can easily account for a strong peak in the radiothermoluminescence curve.

IV. STABILISATION AND CHARGE TRANSFER

The energy spectrum of the charged particles formed in a condensed phase during radiolysis is extremely broad, extending from the primary electron energy (several MeV)

to a few hundredths of an electron-volt. In the case of photolysis the energy spectrum is very much narrower ($E_e \leq 10$ eV).

It is usually assumed that as a result of collisions the electron rapidly loses its excess energy (in $\sim 10^{-14}$ s) to the level of 1–5 eV, and somewhat more slowly (in 10^{-13}–10^{-12} s) to the level of kT. This excess electron in the process of losing energy (or being thermalised), also known as a "dry" or quasi-free electron, is responsible for a number of physical and chemical processes in the condensed phase[8,108,110]. In the majority of condensed media the quasi-free state of the excess electron is unstable, and the electron is captured (solvated) by the medium. Early capture theories such as the Pekar–Deigen–Davydov polar theory and the "cavity" capture theory are reviewed in Ref.3. More recently the total energy (E_t) of the system (medium + excess electron) has been defined[268,269] as $E_t = E_c + E_m$, where E_c is the electronic component of the total energy, and E_m is the reorganisation energy of the medium (≥ 0). For the quasi-free state, which is described by a plane wave being scattered by the atoms and molecules of the medium, $E_m = 0$, and therefore $E_t = V_0$, where V_0 is the energy level of the bottom of the conduction band of the medium measured from the vacuum level, determined by the relative magnitude of the short-range repulsive forces and the long-range polarisation interaction forces. In the case of a localised electron the wave function is $\psi(R) \propto \exp(-R/R_0)$, where R is the configurational coordinate and R_0 is the radius of the coordination sphere (or cavity). The stability of this state is defined by two necessary conditions:

1) $\partial E_t/\partial R = 0$ for $R = R_0$ (configurational stability), and

2) $E_t(R_0) < V_0$ (energy stability).

Exactly analogous arguments can be applied to the stability of the excited states of a trapped electron. V_0 values of 1.32 and −0.63 eV have been calculated[269] for liquid ^{4}He and Ar respectively, as compared with experimental values of 1.05 and −0.33 eV. According to these values the drift mobility of electrons in these liquids should be 2.2×10^{-2} and 470 cm^2 V^{-1} s^{-1} (in the latter case the electron is, obviously, quasi-free). The satisfactory agreement between calculation and experiment for the parameters of the bound state of an electron in liquid helium is illustrated in Table 3.

Table 3. Calculated and experimental physical parameters of trapped electrons in liquid ^{4}He.[269]

Property	Experiment	Theory
Radius of cavity (0 atm), A	16	15.5
Radius of cavity (20 atm), A	10.5	11.5
Mobility, cm^2 V^{-1} s^{-1}	0.02	0.01
Photo-ionisation threshold, eV	0.9—1.0	0.92
Critical density of liquid for transition to the bound state ($E_t < V_0$), mole cm^{-3}	$(1.5—2.0)\cdot 10^{-3}$	$1.0\cdot 10^{-3}$

The properties of trapped electrons in metal–ammonia solutions, in polar liquids, and in glasses have also been explained successfully[153,155,269–271]. Calculations show that the cavities in which the electron is stabilised have diameters of several Ångstroms. In the theoretical calculations for non-polar alkanes the dipole moment of the C–H bond is used[153,272–274] in place of the dipole moment of the whole molecule (as in the case of polar matrices). In other respects the method of calculation is standard. In polymeric materials the cavities are larger than in alkane glasses, because the width of the singlet in the ESR spectra (which characterises the interaction between the captured electron and the surrounding protons on the surface of the cavity) is narrower in these materials, and the spin–lattice relaxation time is longer.

Experimental and theoretical results on the mobility of electrons in non-polar liquids are reviewed in Refs.8, 9, and 275, in polar liquids in Ref.276, and in solid matrices in Ref.277.

Table 4. Characteristics of an excess electron in non-polar liquids[9].

Liquid	T, K	V_0, eV	μ, cm^2 V^{-1} s^{-1}
Methane	109	0.0	400
Neopentane	293	−0.43	50—70
Ethane	120	0.22	0.01
n-Pentane	293	−0.01—0.04	0.14
Cyclopentane	293	−0.21	1.1
Tetramethylsilane	293	−0.59	90—100

As was pointed out above, the main characteristics of an excess electron in the quasi-free state are the energy of the state with respect to the vacuum level (V_0) and the mobility of the electron (μ). Theoretically, a correlation between these two characteristics can be expected. As a rule, higher values of μ correspond to negative values of V_0 (see Table 4). Mobilities $\mu \geq 10$ cm^2 V^{-1} s^{-1} indicate a stable quasi-free state, whereas lower values ($\mu \leq 1$ cm^2 V^{-1} s^{-1}) indicate stability of the bound (localised) state of the excess electron.

A correlation between V_0, μ, and the yield of free charges G_{fl} has also been demonstrated[278]: for $\mu \geq 50$ cm^2 V^{-1} s^{-1} we find $G_{fl} \cong 1.0$ (see Refs.8 and 279).

Two theoretical models have been used to allow for the thermal energy responsible for the transfer of an electron from a localised state (in systems where such a state is stable) into a quasi-free state. The first model (partial localisation model)[280,281] assumes an equilibrium between electrons in the bound and in the free state. The relationship between the observed value μ and the true mobility μ_0 is given by the formula

$$\mu = \mu_0(1-P), \tag{19}$$

where P is the probability of localisation. The second model[282] treats the medium as a complex conglomerate of two different types of region, one transparent and one opaque to excess electrons, and assumes that the volume fraction of the transparent region is a function of V_0 (see Ref.8).

Experimental measurements[283–286] of μ and V_0 in mixtures of alkanes (neopentane/n-hexane) can be explained satisfactorily by both these models.

Experimental data on μ and V_0 in the solid phase are scarce. The main method of determining V_0 in a solid solution is an indirect (complicated, and laborious) measurement of the ionisation potential of TMPD or tryptophan in different solvents[287–293], using the formula

$$\Delta I = I_g - I_s = -P^+ - V_0, \tag{20}$$

where I_g and I_s are the ionisation potentials in the gas and the solid phase, $P^+ = -e^2/2r_0(1-1/\varepsilon_{opt})$ is the polarisation energy of the cation (and r_0 is its radius), and ε_{opt} is the optical dielectric constant. Tentative results obtained in this way for various glasses frozen at 77 K are given in Table 5.

These results suggest a very high mobility for ice and for the 10 M KOH–H_2O alkaline glass, as has been found experimentally[295]: the Hall (i.e. the true) mobility in these media is $\mu_0 \cong 5$ cm^2 V^{-1} s^{-1}. The increase in mobility at low temperatures is consistent with the motion of electrons by the band mechanism. Unfortunately, mobility measurements by the Hall effect are impossible for the majority of frozen hydrocarbons, and experimental results are confined to the drift mobility.

Table 5. Experimental data used to determine V_0 for some glasses at 77 K.[294]

Glass	ΔI, eV	ϵ_{opt}	$-P^+$, eV	V_0, eV
Methylcyclohexane	0.85	2.28	2.09	1.24
3-Methylpentane	0.85	2.22	2.05	1.20
2-Methyltetrahydrofuran (MTHF)	1.08	2.23	2.06	0.98
Ethanol	1.70	2.08	1.94	0.24
Methanol	1.85	1.97	1.84	−0.01
Ice	2.0	1.78	1.64	−0.36
10 M KOH–H_2O	2.2	1.96	1.83	−0.37

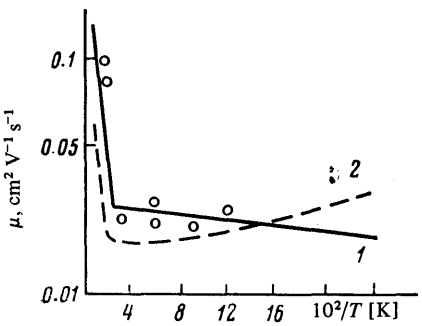


Figure 5. Temperature dependence of mobility: *1*) 3-MP,[296] *2*) MTHF.[297]

Experimental results[296,297] on the mobility of charge carriers in 3-MP and 2-methyltetrahydrofuran (MTHF) are shown in Fig.5. The measurements were by photo-injection of electrons[296] from a TMPD film electrode, or by pulse photolysis[297] of previously γ-irradiated MTHF. The results for the 35–77 K range are interpreted in terms of the Holstein hopping model[298], and those for temperatures below 35 K by the band model. It has been suggested[299] that the transition from hopping conduction to band conduction should occur at the Debye temperature (see Refs.300–302), which for 3-MP and MTHF is close to 35 K, i.e. to the break point in the curves of Fig.5. The reported[296,297] values of μ cannot be compared with the (much lower) values given by the trap-controlled diffusion mechanism for the motion of the carriers[303–306]:

$$\mu = \mu_0 \tau_3 / (\tau_B + \tau_3), \qquad (21)$$

where $\tau_3 \cong 10^{-12}$ s, $\tau_B \cong 10^3$ s at 77 K, and $\mu_0 \cong 1$ cm^2 V^{-1} s^{-1}.

In Ref.307 the drift mobility of electrons in 3-MP at 77 K, measured by injection of high-energy electrons, is given as $\sim 10^{-15}$ cm^2 V^{-1} s^{-1}, which formally agrees with the trap-controlled diffusion mechanism if we take $\mu_0 \tau_3 = 10^{-12}$ cm^2 V^{-1} [138] and $\tau_B = 10^3$ s[138,231,232]. These large discrepancies between the mobility values of a given material require an explanation.

Large discrepancies between experimental values of μ are observed also in polymeric materials. Thus, in the case of polyethylene, which has been investigated intensively[149,150,308–313], μ values between 10^{-4} and 10^{-14} cm^2 V^{-1} s^{-1} have been reported. The higher values (10^{-4}–10^{-6} cm^2 V^{-1} s^{-1}) are usually observed when the chosen measurement method involves the injection of low-energy, "cold" electrons (≲1 eV). Furthermore, the activation energy of the drift mobility (E_a) for these high mobility values is much lower (~0.2 eV) than for the low values of μ obtained after injection of high-energy, "hot" electrons ($E_a \geq 0.5$ eV). These differences between the μ values for hot and for cold electrons are probably associated with the chemical and physical features of the structure with which the excess electrons are interacting. For example, large differences between hot and cold electrons are not observed in PTFE[309,314], whereas in PMMA drift mobilities differing by several orders of magnitude have been reported for the injection of cold[315] and of hot electrons[316], the values being higher for the cold electrons.

It has been found[317] that benzene as the acceptor of a dry electron lowers the yield of solvated electrons (e_s^-) in methanol caused by the two-quantum ionisation of anthracene (or pyrene), but it has no effect on processes induced by laser radiation of wave length corresponding to the absorption band of e_s^-. The authors[317] conclude that the dry electron is not formed in the latter case. Nevertheless we can again postulate that benzene is an effective acceptor of hot dry electrons (two-quantum ionisation of anthracene) but does not react with thermal electrons (see Ref.318). Similar conclusions follow from the work of Kostin and coworkers[319,320].

In general the mobility of an electron in a disordered system depends on the energy of the electron. At some threshold energy E_C' ($E_C' > E_C$) the mobility suddenly increases to a terminal value[321,322] determined only by phonon scattering; under these conditions $\mu_0 \cong 3\lambda$ (where λ is the mean free path of the charge carrier), so that for $\lambda = 30$ Å we have $\mu_0 \cong 100$ cm^2 V^{-1} s^{-1}. For electron energies higher (by ~0.2 eV) than the bottom of the conduction band E_C but not higher than E_C' the motion of the electron can be highly hindered, because some of the space is not available for its motion[323–326]. In this case we are dealing with the continuum problem of the theory of flow[327], in which the mobility is determined by the expression[328]

$$\mu_0 = \frac{eD}{kT} = \frac{1}{6}\left(\frac{e}{kT}\right) a^2 \nu,$$

where a is the lattice parameter. For $a = 3$ Å, $\nu = 10^{15}$ s^{-1}, and $T = 300$ K we obtain $\mu_0 \cong 1$ cm^2 V^{-1} s^{-1}. According to the theory of flow, characteristic mobility values for this mechanism of motion should be in the range 0.01–1.0 cm^2 V^{-1} s^{-1}. Lastly, for electron energies $E_e < E_C$ the motion of the electron takes the form of a series of jumps from trap to trap in the forbidden gap (the hopping conduction mechanism), and $\mu \leq 10^{-5}$ cm^2 V^{-1} s^{-1}.

In disordered systems such as amorphous or partly crystalline glasses and polymers, energy bands are always assumed to be present[321,322,329], because these materials show short-range order in the relative position of atoms and molecules. However, the band edges can be diffuse in this type of material, i.e. they can have tails in which the electrons exist mostly in localised states. Because of the high density of these states their wave functions are able to overlap, and the electron can move by jumping from one localised state to another as a result of interaction with the thermal

fluctuations of the matrix energy. At low temperatures (below the Debye temperature) barrierless tunnelling transitions between localised states become predominant[277,321], causing a sharp change in the temperature dependence of the mobility (see Fig. 5).

In recent years important developments have taken place in the theory of the motion of current carriers in solid amorphous materials (including polymers) in the presence of an external electric field. These developments have been aimed mainly at explaining some special aspects of the drift mobility of electrons and holes determined by the crystal counter method[330–342]. The theory is being developed along two main directions. The earlier approach[343–346] relies on the jump (hopping) mechanism of motion of the electron in amorphous dielectrics, assuming the following distribution of jump times:

$$\psi(t) \propto t^{-(1+\alpha)}, \qquad (22)$$

where α is a constant ($0 < \alpha < 1$). This is the Scher–Montroll stochastic jump model[343]. The function (22) is quite different from the exponential function $\psi(t) \propto \exp(-at)$, used in the classical (diffusion) jump theory, in which the average jump time is assumed to be $t_{aver} = a^{-1}$. A not very convincing account of this theory is given in Refs. 347 and 348. Several critical comments on the Scher–Montroll model are made in Refs. 349–354.

In the second approach the motion of the electron is treated by the classical band model in the presence of a continuous distribution (in energy) of charge traps[355–364]. The equivalence of these two approaches has been demonstrated by several workers[345,359,361,365]. The special features of the non-gaussian diffusion and drift of charge carriers in amorphous matrices are extremely important, because they give a correct formulation of the early stages in the recombination of isolated ion pairs[367] as well as explaining the shape of the initial portion of the current decay curve after irradiation[118,119,368].

Perlman and Bamji[369] stress the need for the utmost care in interpreting experimental results obtained by the crystal counter method in polymers (especially in polyethylene).

One of the models proposed for the motion of a solvated electron e_S^- in a liquid may also find application in the solid state. This is the so-called configuration coordinate model of the motion of e_S^- by diffusion[370–372]. According to this model the orientation polarisation function is arbitrarily fixed, and the total energy E is calculated. A diffusion jump between states with an orientation polarisation function for which the total energy E is a minimum is treated as a continuous change in the polarisation P between the values P_0 and P_1, such that

$$P_u(r) = (1-u)P_0(r) + uP_1(r),$$

where u can vary from 0 to 1.

In full agreement with experiment, the calculated activation energy for the motion of the electron in ice is 0.16 eV. This model avoids the discrepancy with experimental values of the activation energy for electrical conduction found in the earlier models. Thus, in the transition

$$e_s \rightarrow e^- + \text{full orientation relaxation}$$

the activation energy for water is ~0.5 eV. If on the other hand we assume a vertical transition (i.e. a transition in which the orientation is not perturbed) the activation energy is even higher, and coincides with the energy of the optical transition (usually ≥ 1 eV).

The above model is based on the rotation of the molecular dipoles. It is difficult to believe that this rotation can take place at 77 K. However, at room temperature the mechanism may be generally applicable, especially in the case of polymeric materials. The presence of dipoles (due to various structural imperfections and chemical impurities) even in non-polar polymers has been demonstrated by measurements of pyroelectric properties[373]: it is now accepted that substantial changes in dipole orientation can occur even below the glass transition temperature. Thus the conditions in polymers at room temperature are not inconsistent with the proposed mechanism of the drift mobility of a trapped electron in a condensed phase.

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During the preparation of this review several new publications have appeared, with critical comments on many of the topics discussed above. We shall briefly discuss the most important of these.

The validity of the classical ideas on the diffusion and drift of charged particles in interpreting the results of electron trapping measurements and pair recombination in a condensed phase is challenged[374], in spite of the allowance for non-gaussian diffusion of electrons in amorphous matrices[367,375–383]. An attempt is also made[379,380,382] to explain the kinetics of the disappearance of ion radicals in frozen organic glasses in terms of the Scher–Montroll model rather than by the tunnel effect.

A study of the photo-ionisation of TMPD in non-polar solvents has led to the conclusion[384,385] that the precursor of the free electron is not an ion pair but an excited state of the solute molecule. This result is directly relevant to the problem of the contribution of electrons from isolated pairs to the electric current (see Refs. 104, 127, 386).

The influence of the dose ($\leq 10^3$ Rad) on the induced electrical conductivity during pulsed (~50 ns) irradiation of crystalline ice is discussed in Ref. 387, mainly in terms of the formation of free OH radicals. These results agree very well with those of Nikol'skii and coworkers[262], who showed that in polyethylene electron capture (mainly on radicals) begins at doses as low as $\sim 10^5$ Rad. It is suggested that the formation of stabilised electrons, characterised by the i.r. absorption spectrum, involves electron capture by pre-existing traps not only in solid[388] but also in liquid polar matrices[389]. The possibility of explaining the "blue" shift of the absorption spectrum of a trapped electron in terms of its motion within the ion pair is discussed[390]. However, Rice[391] believes that in molecular frozen glasses the migration of trapped electrons is unlikely, though such migration has been demonstrated experimentally in frozen alcohols[392] with observation times ≤ 750 ns (see also Ref. 393).

The lowest reported values ($\leq 3 \times 10^{-13}$ cm^2 V^{-1}) of $G\mu_0\tau_3$ have been observed in polar polymers[114,120]. This has been interpreted[126] as evidence that the conduction is due to hot electrons with energy ≤ 10 eV, and a far-reaching analogy between RPEC and electrical breakdown in dielectrics has been proposed[394] (see also Refs. 104 and 120). Vaisburd's model of the electrical conduction induced in dielectrics by powerful electron beams[395,396] should also be mentioned here.

We have been unable, through lack of space, to deal adequately with the generation of current carriers from excited neutral states of the polymer molecule or from complexes, which plays a fundamental role in photolysis[397] and may also be important in radiolysis. The study of these states has been made much easier by our improved understanding of spin effects in the elementary processes of high-energy chemistry, due mainly to the work of Frankevich and coworkers (see review articles in Refs. 398 and 399). The energy structure of ionised and excited states in organic molecular crystals is now known in great detail[400–402].

Therefore we can hope for similar advances, in the near future, in our understanding of disordered organic matrices, including polymers.

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Oxidation of Alkyl Derivatives of Aromatic Hydrocarbons by Transition Metal Salts

I.P.Beletskaya and D.I.Makhon'kov

The oxidation reactions of aromatic compounds and their alkyl derivatives under the influence of salts of variable-valence transition metals are examined.
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I. INTRODUCTION

Reactions involving the oxidation of aromatic compounds by transition metal salts have attracted much attention in recent years. These reactions, which have come to be called "stoichiometric oxidation", make it possible to obtain in many instances mainly one of the oxidation products, i.e. to "functionalise" aromatic compounds selectively[1].

Substituted benzenes and condensed aromatic systems without substituents capable of being oxidised have always given rise to products with functional groups, which are linked directly to the aromatic nucleus. Another important class of substrates are alkyl derivatives of aromatic compounds, which yield, on oxidation, the products of monosubstitution in the α-position of the side chain as well as the corresponding oxo- and carboxy- derivatives, apart from the compounds of the type mentioned above.

There is an extensive literature on problems of liquid-phase and stoichiometric oxidation and the number of original publications in this field continues to increase rapidly. This review summarises data on the oxidation of aromatic compounds and their alkyl derivatives by variable valence metal ions (the literature up to the middle of 1979 is included). We shall not consider oxygen-containing metal compounds in the highest oxidation states (such as the salts of chromic and manganic acids), which have been used for a long time and which have been fairly thoroughly investigated, as well as substrates which exhibit specific features in oxidation processes (phenols, aromatic alcohols, amines, etc.), with the exception of those cases where the oxidation involves only the aromatic system and (or) alkyl substituents in these compounds.

II. GENERAL MECHANISMS OF OXIDATION BY METAL SALTS

Silver(II), copper(II), palladium(II), cobalt(III), manganese(II), iron(III), thallium(III), lead(IV), and cerium(IV) compounds used as oxidants can be divided into two groups: one-electron and two-electron oxidants; their standard electrode potentials vary within wide limits [the values of E^0 (V) are listed below]:

Ag^{2+}/Ag^{+} 1.91	$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ 0.36
Co^{3+}/Co^{2+} 1.808	Cu^{2+}/Cu^{+} 0.167
Ce^{4+}/Ce^{3+} 1.61	Pb^{4+}/Pb^{2+} 1.694
Mn^{3+}/Mn^{2+} 1.509	Tl^{3+}/Tl^{+} 1.252
Fe^{3+}/Fe^{2+} 0.771	Pd^{2+}/Pd^{0} 0.987

One should note that a characteristic feature of variable-valence metal compounds is the occurrence in solutions of complex equilibria involving hydrolytic and complex formation reactions and the formation of dimers and polymers, which alter the oxidation-reduction potentials and the activities of the above compounds. Depending on the structural characteristics of the salt, the specific features of the metal and its ligand environment, the type of aromatic compound, and the conditions (for example, temperature, and the nature of the solvent), the oxidant and the substrate can interact via several different mechanisms.

1. Electron transfer from the π-electron system of the substrate to the metal atom with formation of a radical-cation of the aromatic compound. This process can proceed after the inclusion of the substrate molecule in the coordination sphere of the metal (inner-sphere transfer, *a*) or without the breakdown of this sphere (outer sphere transfer, *b*):

$$CH_3ArH + M^{n+} \begin{cases} \xrightarrow{a} [CH_3ArH \ldots M^{n+}] \rightarrow [(CH_3ArH^{\cdot+}) \ldots M^{(n-1)+}] \\ \xrightarrow{b} CH_3ArH^{\cdot+} + M^{(n-1)+} \end{cases} \quad (1)$$

2. Homolytic decomposition of the substrate–oxidant complex with simultaneous transfer of an electron and a ligand and the formation of a benzyl type radical (2*a*) or the product of radical addition to the substrate (2*b*):

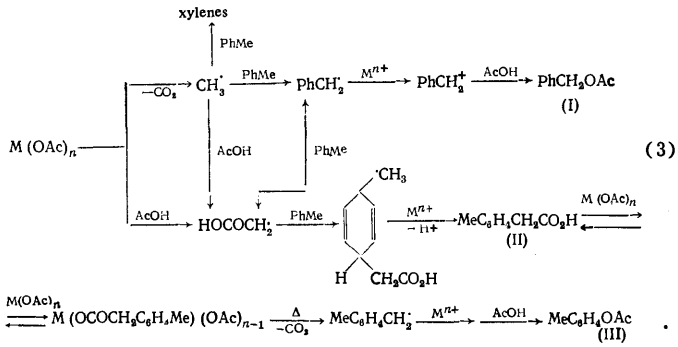
$$HArCH_3 + M^{n+}X^- \begin{cases} \xrightarrow{a} HArCH_2^{\cdot} + HX + M^{(n-1)+} \\ \xrightarrow{b} H_3CAr^{\cdot}\!\!\begin{array}{l}H\\X\end{array} + M^{(n-1)+} \end{cases} \quad (2)$$

Processes of this kind appear, in particular, in oxidation by complex cerium(IV) salts, copper(II) and iron(III) halides, etc. (see below).

3. Oxidation initiated by free radicals arising in the decomposition (photochemical or thermal) of the oxidant molecule (usually the metal carboxylate).

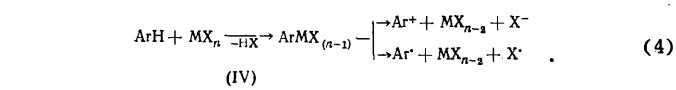
Depending on the nature of the metal, the structure of the carboxylate ion, and the solvent used, such decomposition is accompanied by decarboxylation leading to alkyl or aryl radicals and (or) the formation of carboxyalkyl radicals. Both types of radicals initiate the process, giving rise to alkylation, carboxyalkylation, acyloxyalkylation, etc. products in proportions determined by the specific characteristics of the intermediates, which can be illustrated by the general mechanism of the oxidation of toluene in AcOH by

lead(IV), manganese(III), and cerium(IV) acetates (for further details, see the appropriate sections of the review):



(3)

4. Metallation of the aromatic substrate with a metal salt and subsequent decomposition of the organometallic compound with formation of an aryl radical or an aryl cation:



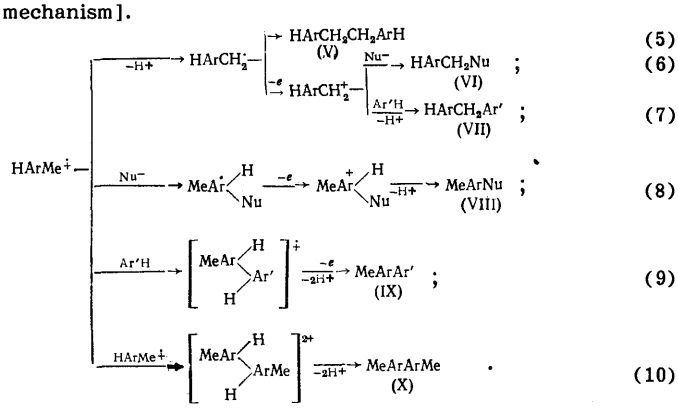
(4)

(IV)

Processes of this type are characteristic of lead(IV), palladium(II), and particularly thallium(III) salts (see below).

Thus the first stage of the reaction of the aromatic substrate with a metal complex leads to the formation of a radical, cation, or a radical-cation, depending on the mechanism. The transformations of radicals on interaction with the metal compounds have been discussed in detail in reviews[2,3]. They are usually terminated either by oxidation via a ligand transfer mechanism [analogous to mechanism (2)] or by oxidation to a cation, which subsequently reacts with a suitable nucleophile (see below).

The fate of the radical-cation formed via mechanism (1) merits a more detailed investigation. In the presence of an alkyl (particularly methyl) group in the molecule, the radical-cation usually loses a proton with formation of a radical of the benzyl type, which is then oxidised to a cation, reacting with an anion or a solvent molecule to form a product of substitution in the α-position of the side chain [mechanism (6)]. When the stability of this radical is high, 1,2-diarylethanes of type (V) are also formed. In a weakly nucleophilic medium (in the presence of strong acids or in the heterophase oxidation in an excess of the substrate) the cation formed attacks a second substrate molecule with formation of diarylmethanes via mechanism (7) [in principle the formation of compound (VII) is also possible as a result of the oxidation of the radical adduct comprising $HArCH_2^{\cdot}$ and $HArCH_3$, but the available literature data concerning the high regioselectivity of reaction (7) are inconsistent with this mechanism].



(5)
(6)
(7)
(8)
(9)
(10)

An alternative reaction pathway involves direct attack by an anion or a solvent molecule on the radical-cation and the formation of the ring-substituted product (VIII) via mechanism (8). In the absence of alkyl substituents from the substrate molecule or when factors (for example, steric factors) hindering the formation of a benzyl radical operate, this reaction pathway becomes dominant in highly nucleophilic media. The dimerisation of the radical-cation or its interaction with another molecule of the aromatic compound leads to the formation of biphenyl derivatives via mechanisms (9) and (10). The oxidative dehydrodimerisation pathway, leading to products of types (VII), (IX), (X), depends on the structure and on the distribution of the positive charge (in a substituted or unsubstituted position of the aromatic ring) of the initial radical-cation. Reactions of this type are frequently accompanied by polymerisation and disproportionation.

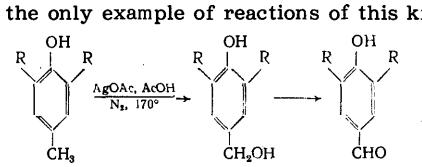
Reactions (5)–(10) frequently take place simultaneously, but the choice of conditions (variation of the temperature parameters and solvents, the introduction of nucleophilic additives, strong acids, complex-forming agents, etc.) makes it possible to drive the process in the required direction and to obtain a product with a high selectivity.

The specific features of such processes are considered below in relation to various types of oxidants in conformity with the classification adopted for the latter (see above) in order of their decreasing oxidation-reduction potentials.

III. VARIABLE-VALENCE METAL IONS AS OXIDANTS FOR ALKYLARENES

1. Silver(I), Silver(II), and Silver(III)

The use of silver(I) salts and Ag_2O for the oxidation of hydroquinones and aldehydes is well known, but the stepwise oxidation of the methyl group of 2,6-dialkyl-*p*-cresols is apparently the only example of reactions of this kind†.



R = t-Bu or Me.

Silver(II) compounds are strong oxidants, but their use in organic syntheses is fairly limited[6].

Many oxidation processes take place successfully in the $Ag^+–S_2O_8^{2-}$ system, but do not occur in the absence of silver ions. As suggested previously, the role of the latter is not exhausted by the formation of $SO_4^{\cdot-}$ radical-anions. The latest studies[7,9] have shown that Ag^{2+} ions make an appreciable contribution to the oxidation of the substrate. The process involves a series of oxidation-reduction reactions:

$$S_2O_8^{2-} + Ag^+ \rightarrow SO_4^{2-} + SO_4^{\cdot-} + Ag^{2+} ;$$
$$SO_4^{\cdot-} + RH \rightarrow SO_4^{2-} + R^{\cdot} + H^+ ;$$
$$SO_4^{\cdot-} + Ag^+ \rightarrow SO_4^{2-} + Ag^{2+} ;$$
$$Ag^{2+} + RH \rightarrow Ag^+ + RH^{+\cdot} .$$

†There exist also patent data[5] concerning the oxidation of toluene to benzyl alcohol by passing oxygen through a solution in acetic anhydride containing catalytic amounts of silver acetate.

The Ag^{2+} and $SO_4^{\cdot-}$ species act in these reactions as oxidants with different selectivities[8] and the contribution of the oxidation by Ag^{2+} ions increases with increasing Ag(II)/substrate ratio.

The stability of organic silver(II) complexes increases appreciably with increasing acidity of the medium and in the presence of nitrogen-containing ligands[6,7]. Thus bis(2,2-bipyridyl)silver(II) peroxydisulphate in acetic acid acetoxylates alkylarenes in the ring and (or) in the α-position of the side chain[7,8] via mechanism (11) in ~300% yield with respect to silver(II) (two oxidants are involved in the reaction):

$$3ArH + 2Ag(II) + 2S_2O_8^{2-} + 3AcO^- \rightarrow 3ArOAc + 2Ag(I) + 4SO_4^{2-} + 3H^+ \quad (11)$$

In addition, methylbenzenes give rise to small amounts of benzaldehydes. Silver(II) salts without the $S_2O_8^{2-}$ anion react analogously[10]. Silver(II) picolinate (pyridine-2-carboxylate) $Ag(pic)_2$ and bis(2,2-bipyridyl)silver(II) trifluoromethanesulphonate $Ag(bipy)_2(CF_3SO_3)_2$ oxidise *p*-methylanisole to a mixture of the corresponding alcohol and aldehyde (3:1) in quantitative yields. The rate of oxidation increases greatly in the presence of potassium acetate, which has been attributed[10] to the buffer effect of the acetate ion [see mechanism (11)] and (to a greater extent) to the increased solubility of the silver(II) complexes in the presence of potassium acetate.

The results of the competitive oxidation of *p*-substituted toluenes yield $\rho = -3.4$ and the kinetic isotope effect, which is absent in the acetoxylation of the ring, amounts to 5.9 for α, α, α-d_3-*p*-methoxytoluene. Thus, in the absence of the peroxydisulphate ion, the oxidation of arylmethanes involves electron transfer with formation of a radical-cation [mechanism (1)], which then loses a proton in the rate-determining stage of the reaction[10].

Silver(II) picolinate can also be used in neutral media[11,12]: the oxidation of alkylarenes by an aqueous suspension of $Ag(pic)_2$ gives rise to carbonyl compounds[11], while the reaction with PhMe in dimethyl sulphoxide (DMSO) at 65 °C[12] makes it possible to obtain $PhCH_2OH$, PhCHO, and $PhCO_2H$ in succession, depending on the amount of the oxidant (the yields are 60, 15 and 45% respectively in each case).

In principle, the reactions of silver(II) salts may involve the participation of silver(III) species formed via the reaction

$$2Ag(II) \rightleftarrows Ag(I) + Ag(III).$$

However, it has been shown that this equilibrium is greatly displaced to the left and silver(III) plays an insignificant role in the processes occurring, for example, in the $Ag^+-S_2O_8^{2-}$ system[8]. Such reactions follow second-order kinetics, which is inconsistent with the involvement of silver(III).

At the same time it is known that stable silver(III) compounds can be obtained in the form of complexes of AgX_3 ($X = HSO_4$, NO_2, ClO_4, or OH) with biguanidine, ethylenebiguanidine, etc. and also in the form of the oxide Ag(I).$\cdot$Ag(III)O_2.[13] A solution of Ag_2O_2 in mixtures of aqueous acids (H_3PO_4, AcOH) oxidises methylarenes to the corresponding aldehydes in fairly high yields (54% for PhMe and 90% for *p*-MeC_6H_4OMe).[14] It is of interest that diphenylmethane is inert under these conditions, while the yield of Ph_2CO in the oxidation in the $Ag(pic)_2-H_2O$ system is 43%.[11]

It is noteworthy that, according to Crivello's data[15], Ag_2O_2 in a trifluoroacetic acid–trifluoroacetic anhydride mixture oxides aliphatic hydrocarbons and in the case of adamantane, for example, gives rise to 1-adamantyl trifluoroacetate in 98% yields.

2. Cobalt(III)

Like silver(II), cobalt(III) is a powerful oxidant in acid media. A study of the Co(III)/Co(II) oxidation-reduction potential in aqueous solutions of HCl, H_2SO_4, AcOH, and $HClO_4$ showed that the potential of the above pair decreases with increasing acid concentration[16].

Like Ag_2O_2, cobalt(III) hydroxide in aqueous solutions of acetic and phosphoric acids oxidises methylarenes to the corresponding aldehydes in yields ranging from 25% (mesitylene) to 95% (*p*-methylanisole). Toluene is inert under these conditions[16]. An advantage of this process is its relatively high selectivity.

Cobalt trifluoride oxidises benzene at 200–250 °C to a mixture of cyclic polyfluoro-derivatives (25–30 products), mainly octafluorocyclohexanes[18]. It has been shown that the first stage of the reaction is electron transfer with formation of a radical-cation[18]. Under the same conditions, potassium tetrafluorocobaltate gives rise to a mixture of polyfluorocyclohexenes[19]. The proportions of the products in the case of the tetrafluorocobaltates of other alkali metals depend greatly on the nature of the cation[20]. The reaction requires increasing temperatures on passing from lithium (100–130 °C) to caesium (250 °C) and only in the last case does the reaction mixture contain, apart from the products of the successive saturation of the aromatic system (mainly 3,3,6,6-tetrafluorocyclohexadiene), polyfluorobenzenes, including hexafluorobenzene (6%).[20] It remains obscure how the variation of the cationic component influences the structure of the salt and its reactivity. However, it is of interest that, according to the data of Edwards et al.[20], potassium hexafluorocobaltate is inert under the same conditions.

The study of the heterogeneous oxidation of toluene and xylenes with potassium 12-tungstocobaltate(III) $K_5[CoO_4W_{12}\cdot O_{36}].H_2O$,[21] which gives rise to mixtures of diarylmethanes, monoaldehydes, and the corresponding alcohols, showed that the radical-cation of the aromatic compound is formed as a result of an outer-sphere electron transfer [mechanism (1*b*)]. The subsequent transformations of the radical-cation proceed via mechanisms (6) and (7).

Under homogeneous conditions (AcOH–H_2O), the reactions of potassium 12-tungstocobaltate(III) with aromatic compounds are in many respects analogous to the anodic oxidation processes and reactions involving silver(II) salts[22]. Thus anisole, biphenyl, and naphthalene gives rise to aromatic ring acetoxylation products in the presence of potassium acetate, the oxidation of 4-fluoroanisole in the same system being accompanied by the substitution of fluorine by the acetoxy-group. Mesitylene is also partly acetoxylated in the ring under these conditions (as in anodic oxidation), although in the reaction with cobalt(III) carboxylates, even in the presence of potassium acetate, only α-acetoxylation is observed (see below). Toluene, xylenes, and hexamethylbenzene give rise to only α-hydroxy- and acetoxy-derivatives in the absence of potassium acetate, while 4-methoxytoluene also forms the dehydrodimer 2-(4-methoxybenzyl)-4-methylanisole. In the presence of potassium acetate the rate of oxidation falls and oxidative coupling is fully suppressed by toluene and xylenes give rise also to acetoxymethylation products [see mechanism (3)] whose yield increases sharply in anhydrous acetic acid. The isotope effect in the oxidation of α,α,α-d_3-*p*-methoxytoluene, amounting to ~6, has been interpreted[22] as evidence for a reaction mechanism involving the concerted transfer of an electron and the proton of the α-C–H bond to the oxygen atom of the heteropolyion as the rate-limiting stage.

However, simpler cobalt(III) salts—the perchlorate and carboxylates—are frequently used. In aqueous $HClO_4$ cobalt(III) perchlorate steadily oxidises benzene with formation of a mixture of *p*-benzoquinone, muconic acid, and its lactone[23]. The reaction kinetics obey the equation

$$-\frac{d[Co(III)]}{dt} = \left(k_1 + \frac{k_2}{[H^+]}\right)[Co(III)][PhH].$$

This has been interpreted[23] as evidence for the involvement in the process of two types of oxidising species—the aquo-complex of cobalt(III) and the more active hydroxy-complex $Co(OH)^{2+}$.

In the $HClO_4$–H_2O–MeCN system cobalt(III) perchlorate oxidises alkylarenes to mixtures of the corresponding alcohols, aldehydes, and acids. According to the data of Cooper and Waters[24], the reaction of toluene involves outer-sphere electron transfer and is accelerated with increase of the concentration of acetonitrile in the solvent. In the mixture with 50% MeCN the products resulting from the oxidation of the methyl group are formed exclusively, but in the presence of higher contents of acetonitrile the formation of methylbenzophenones and benzylbenzaldehyde—the products of the reaction of toluene with the benzyl radical arising in the oxidation of benzaldehyde—was also noted. The reactivity of the substrates increases in the sequence p-$NO_2C_6H_4CH_3 < PhCH_2CH_2Ph \cong PhMe \cong PhEt < Ph_2CH_2 <$ t-$BuC_6H_4CH_3 < Ph_2$.

It is of interest that benzyl alcohol is oxidised faster under these conditions than diphenylmethanol. This phenomenon has been attributed[24] to the steric characteristics of the complexes formed on direct coordination of alcohols to a cobalt atom; it is suggested that the electron transfer takes place in this instance via an inner-sphere mechanism [see mechanism (1*a*)].

The oxidation of toluene by cobalt(III) perchlorate is appreciably accelerated when aliphatic acids are introduced into the reaction mixture[25].

The slow electron transfer from the toluene molecule is replaced under these conditions by the rapid abstraction of hydrogen from the methyl group by the alkyl radical formed via the reaction

$$RCOOH + Co(III) \rightarrow R^{\cdot} + CO_2 + Co(II) + H^+ . \qquad (12)$$

The benzyl radical is rapidly oxidised further via mechanism (6) and partly dimerises with formation of bibenzyl [mechanism (5)].

Aryl-substituted aliphatic acids are oxidised by cobalt triacetate (CTA) with formation of a radical-cation [mechanism (1)] and then a benzyl-type cation [mechanism (6)].[26] Under these conditions, γ-phenylbutyric acid gives rise to an intramolecular oxidation product—γ-phenylbutyrolactone:

$$PhCH_2(CH_2)_2CO_2H \xrightarrow[-H^+]{2Co(III)} PhCH(CH_2)_2CO_2H \xrightarrow[-H^+]{} \text{lactone} .$$

In the presence of LiCl or trifluoroacetic acid the yield of the lactone increases from 25 to 60%.[26]

In the presence of arylacetic acids the radical-cation formed is decarboxylated and gives rise to substituted benzyl acetates, in conformity with mechanism (6):[26]

$$[ArCH_2CO_2^-]^{\cdot} \xrightarrow{-CO_2} ArCH_2^{\cdot} \xrightarrow{Co(III),\ AcO^-} ArCH_2OAc .$$

Cobalt(III) carboxylates oxidise alkylbenzenes to the corresponding benzyl carboxylates[26–37] and the ligand environment of Co^{3+} plays a significant role in this reaction, whose first stage is believed[27–30] to involve the insertion of the substrate in the inner coordination sphere of cobalt(III). Neutral ligands, which strongly coordinate cobalt(III)—bipyridyl, pyridine, and acetonitrile—lower the rate of reduction of cobalt(III) with increase of their concentration in the reaction mixture up to the complete suppression of the oxidation process[27]. When water is added, the rate of reduction of cobalt(III) initially increases and then falls to the initial value at $[H_2O] > 2.2$ M. With increase of the size of the carboxylate anion, the electron transfer of the cobalt(III) atom is suppressed and the main reaction pathway becomes the decomposition of the oxidant [via a mechanism analogous to mechanism (12)], whose contribution is 82% for pelargonic acid and 100% for isobutyric acid[27]. The ligand effect is in this case attributed to the steric hindrance in the formation of the Co(III)–RH complex and not to the decrease of the oxidation potential of cobalt(III).[27]

The addition of potassium acetate accelerates the oxidation of toluene by CTA in acetic acid[31,32] but has little influence on the proportions of the products (31% $PhCH_2OAc$, 7% PhCHO, and 2% of bibenzyl are formed at 37 °C [31]). An increase of temperature lowers the overall yield of products and is accompanied by the formation of small amounts of xylenes and methylbenzyl acetates [see mechanism (3)]. The thermolysis of CTA in acetic acid is accompanied by the liberation of CO_2 and small amounts of methane and is almost completely suppressed in the presence of aromatic substrates[31], which differs sharply from the behaviour of manganese(III), lead(IV), and cerium(IV) acetates under analogous conditions (see below). On oxidation with CTA, 2-methylnaphthalene gives rise also to 1-acetoxy-2-methylnaphthalene (18%) apart from the products formed as a result of the oxidation of the methyl group (~50%) [see mechanism (8)].[31]

The kinetics of the oxidation of aromatic compounds by cobalt triacetate are described by the following equation according to a series of data[28,29,30]:

$$-\frac{d[Co(III)]}{dt} = k_{obs}[ArH][Co(III)]^a[Co(II)]^{-1},$$

where k_{obs} is independent of the association energy of the C–H bond of the substrate but is correlated with its ionisation potential and its ability to coordinate to the cobalt(III) ion[28].

In the presence of O_2 the kinetic parameters of the reaction remain unchanged[33], but the products are the corresponding aldehydes and acids. Thus the presence of oxygen does not affect the rate-determining stage of the reaction—the loss of a proton by the radical-cation formed via mechanism (1). The reactivity of arylalkanes decreases in the sequence p-xylene > PhMe > PhEt > PhPr-iso > p-ClC_6H_4Me. [31,32]. The rate of reaction increases in the presence of AcO^- and decreases as cobalt(II) accumulates in the reaction mixture[28,32]. The latter factor demonstrates, in particular, the possibility of electron transfer in reaction (1).

Another explanation of the inhibiting effect of cobalt(II) involves the formation of dinuclear Co(III)–Co(II) complexes with a greatly reduced oxidation-reduction potential[27–35]. According to Kawai and Kamiya[34], the addition of manganese, platinum, and cerium acetates in both the highest and lowest oxidation states also reduces the oxidising capacity of cobalt(III) up to the complete disappearance of activity for certain molar proportions. The inhibition sequence is as follows: Mn(II) > Mn(III) ≅ Ce(IV) > Cu(II). The formation of polynuclear cobalt(III) complexes has also been confirmed by spectroscopic methods[34]. However, it is of interest that the Co(III)–Co(II) combination, which is inactive in the oxidation of toluene, exhibits the same activity as cobalt(III) in the oxidation of 1-methylnaphthalene[34].

The activity of cobalt(III) increases appreciably in the presence of halide ions (Cl^- and Br^-) [31,38-40] and also organic bromo-derivatives—bromobenzene, dibromoethane, butyl bromide, etc.[38] It has been shown[39] that in the presence of an excess of chloride ions in the CTA–AcOH system the highly reactive hexachlorocobaltate(III) anion is formed and decomposes rapidly with formation of Cl_2 and $CoCl_2$. In the presence of smaller amounts of Cl^- the formation of mixed cobalt(III) acetate-chloride complexes, which also exhibit an enhanced reactivity, is more likely. The existence of such complexes has been confirmed by spectroscopic data[31].

The main product of the oxidation of toluene by CTA in the presence of LiCl is benzyl chloride, but, with increase of the Cl^- concentration, its yield falls as a consequence of the formation of ring-chlorination products[31]. The reaction of 2-methylnaphthalene proceeds analogously[31]. On the other hand, in the presence of Br^-, toluene gives rise exclusively to benzyl bromide[40].

It is of interest to note that the interaction of CTA with Br^- in acetic acid at 70 °C is complicated, which is believed[41] to be due to the presence in solution of two forms of CTA—$[Co(AcOH)_6]^{3+}(OAc)_3$ and $[Co(OAc)_3(AcOH)_3]$ in proportions of ~1:1. It has been suggested that the oxidation of Br^- takes place after the exchange of the ligands of the cobalt atom from bromide, the first form reacting rapidly with Br^- and the second form slowly, i.e. the rate of reaction is limited by the ligand exchange stage.

On the other hand, X-ray diffraction studies[42] have shown that CTA has the structure of an O-centred trimer $[Co_3O(OAc)_6(AcOH)_3]OAc$ containing two types of acetoxy-groups—bridging and chelate, which may also be the cause of the existence of two stages in the reaction of cobalt(III) with Br^-.

The formation of benzyl bromide in the oxidation of toluene in the presence of Br^- is attributed[33,41] to the simultaneous reactions involving the bromination of the substrate by the liberated bromine and the "cobalt bromide" complex via the mechanism

$$\mathrm{Co\,(III) + Br^- \rightleftarrows [Co\,(II)\ldots Br^{\cdot}]}\ ;$$
$$\mathrm{RH + [Co\,(II)\ldots Br^{\cdot}] \rightarrow Co\,(II) + R^{\cdot} + Br^- + H^+}\ ;$$
$$\mathrm{R^{\cdot} + [Co\,(II)\ldots Br^{\cdot}] \rightarrow RBr + Co\,(II)}\ .$$

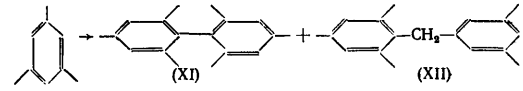
The Co(III)–Br^- system is widely used as a catalyst in industrial liquid-phase oxidation of alkyl derivatives of aromatic compounds, but the mechanism of the so-called cobalt bromide catalysis is still controversial (see, for example, Emanuel' [1] and Zakharov[43]).

The oxidising properties of cobalt(III) increase appreciably in the presence of strong acids. The addition of H_2SO_4, CCl_3CO_2H, $HClO_4$, H_3PO_4, and BF_3 increases the rate of oxidation of alkylarenes by cobalt(III) acetate so much that these reactions can be carried out at room temperature[36]. Thus, in the oxidation in acetic acid in an inert atmosphere, the reaction products are substituted benzyl acetates, while in the presence of O_2 they are aldehydes and acids[36]. The activating effect of strong acids has been explained[36,44] by the destruction of the cobalt(III) cluster complexes (see above), by the formation of monomeric species, and by the enhanced electrophilic properties of the metal atom. However, one should note that the increase of the concentration of strong acid increases the activity of cobalt(III) so much that the oxidation of the solvent (acetic acid) becomes a competing process at 25 °C.[36]

The benzyl acetate formed in the oxidation of toluene in the CTA–AcOH–$HClO_4$ system reacts with toluene when the temperature is raised (up to 114 °C), giving a mixture of phenyltolylmethanes[45]. Under these conditions, other alkylbenzenes (PhEt, p-$ClC_6H_4CH_3$, xylenes, and mesitylene) also give rise to mixtures of diarylmethanes and small amounts of monoaldehydes, whose relative content increases in the presence of oxygen[45].

Trifluoroacetic acid (TFAA) occupies a special place among acid activators. The formation of complexes involving charge transfer between cobalt(III) and the aromatic substrate has been discovered in TFAA solutions[46]. The dissociation products of such complexes are cobalt(II) and the substrate radical-cation [see mechanism (1)] stabilised by the TFAA.[46] The efficiency of such stabilisation is so great that it makes it possible to obtain well resolved EPR spectra of the radical-cations even in the case of the relatively unstable dialkylbenzenes[46].

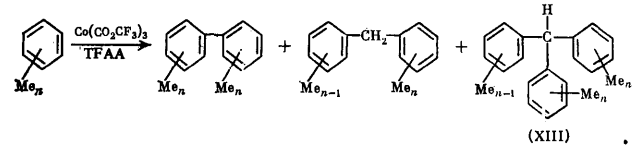
On the other hand, the breakdown of the cluster structure of the CTA and the ligand exchange in the interaction between CTA and TFAA are fairly slow, so that solutions of cobalt(III) acetate and trifluoroacetate in TFAA exhibit different reactivities[48,49]. The reaction of mesitylene with cobalt triacetate in TFAA proceeds via the mechanism



(13)

and yields 2% of compound (XI) and 20% of compound (XII), while in the analogous reaction with $(CF_3CO_2)_3Co$ the yields of compounds (XI) and (XII) are respectively 16 and 9%. It is of interest that the yield of compound (XI) increases in the latter case with decrease of temperature and reaches 41% at −12 °C with simultaneous formation of 21% of nonamethyl-*m*-terphenyl.[49] When reaction (13) is carried out in the $(CF_3CO_2)_3Co$–TFAA–$C_2Cl_2H_4$ system (80 °C), the product ratio (XI):(XII) varies from 0 to 1.8 as the TFAA concentration rises from 0 to 100% [in pure $C_2Cl_2H_4$ and in mesitylene compound (XII) is formed in 28% yield].[49]

The oxidation of toluene, xylenes, pseudocumene[49], and durene[48] proceeds via the general mechanism



The biaryls (X) are hardly formed in the case of toluene, p-xylene, and durene, while the yield of compounds (XIII) and (X) is a maximum for *m*-xylene and pseudocumene.

The use of this reaction for the oxidation of mixtures of aromatic hydrocarbons[48] can be regarded as a valuable method of synthesising asymmetric biaryls and diarylmethanes (see, for example, Kozhevnikov and Matveev[50]). Under analogous conditions, benzene is readily oxidised to phenyl trifluoroacetate (the yield reaches 90%,[51,52] falling in the presence of an excess of benzene owing to the formation of a mixture of polyphenyls). Chlorobenzene and trifluoromethylbenzene are formed similarly albeit in lower yields[52].

The oxidation of aromatic substrates by cobalt trifluoroacetate in the presence of inorganic anions makes it possible to obtain in high yields the products of nucleophilic substitution in the aromatic ring via mechanism (8).[54] Thus the oxidation of benzene in the TFAA–LiCl–$Co(OCCF_3)_3$ system yields a mixture of phenyl trifluoroacetate and chlorobenzene (~1:1) for the ratio $Co(III)/Cl^- = 1$. An increase of the Cl^- concentration fully suppresses trifluoroacetoxylation, while the yield of chlorobenzene reaches 90%. Bromo- and iodobenzenes can be obtained analogously but in lower yields[53].

The oxidation of toluene under these conditions leads to a complex mixture containing chlorotoluenes, benzyl chloride, and compounds of types (X), (VII), and (XIII).[53] It is of interest that in the presence of air the main products are chlorotoluenes, while in an inert atmosphere benzyl chloride is mainly formed. The reaction thus involves processes described by mechanisms (5)–(10). The reactions of $Co(OCOCF_3)_3$ in the presence of F^-, CN^-, NO_2^-, and NO_3^- have also been studied[53].

In aqueous solutions of trifluoroacetic acid in the presence of halide ions, even toluenes containing strongly electron-accepting substituents can be oxidised by cobalt(III) acetate. Thus *p*-toluic acid is oxidised in the $CF_3COOH–H_2O–Hal$ system at room temperature and gives rise to the products of the oxidative halogenation of the aromatic ring and (or) the side chain[54,55]. In the presence of KCl the main product is 3-chloro-4-methylbenzoic acid, while the reaction in the presence of NaBr gives rise mainly to 4-carboxybenzyl bromide[54]. In the latter case the side products are hydroxy-, acetoxy- and trifluoroacetoxy-methylbenzoic acids. 4-Hydroxymethylbenzoic acid—a valuable monomer for the synthesis of polymeric materials, which are superior as regards many parameters to the analogous materials based on terephthalic acid—can be obtained by hydrolysing the above reaction mixture[55].

The use of cobalt(III) chelates (acetylacetonate, benzoate, δ-quinolinate, etc.) makes it possible to carry out the reaction in non-polar solutions[56–58]. Thus the oxidation of 2,6-xylenol with cobalt(III) salicylideneaminates in toluene proceeds via an oxidative coupling mechanism and gives rise to a mixture of 4,4′-dihydroxy-3,5,3′,5′-tetramethylbiphenyl and the corresponding quinone[57]. It has been suggested[54] that the reaction involves the dimerisation of a radical formed via the mechanism

$$CoL_3 + RH \rightleftarrows CoL_2 + R^{\cdot} + HL \quad .$$

The kinetics of the oxidation of cumene by cobalt(III) chelates have been studied[58], but there are no data on the products of this reaction.

3. Manganese(III)

The reactions of manganese triacetate (MTA) in acetic acid with *p*-methoxytoluene[59] or toluene in the presence of NaBr[40] and with alkylbenzenes in the presence of strong acids[36] proceed analogously to the corresponding reactions of cobalt triacetate and are characterised by the same kinetic features i.e. they include the stage of the reversible electron transfer to the metal atom [mechanism (1)].

Like cobalt(III) acetate, manganese(III) acetate oxidises *p*-toluic acid in trifluoroacetic acid in the presence of chloride and bromide ions with formation of products of the oxidative halogenation of the aromatic ring and (or) side chain, but in this instance the reaction in the $Mn(III)–Cl^-$ system leads almost exclusively to a 3-chloro-4-methylbenzoic acid (yield ~100%).[54]

In the absence of activators, the reactions with manganese(III) salts require increased temperatures and are accompanied by radical substitution reactions because of the lower oxidising capacity of the metal ion (Table 1). The thermolysis of manganese(III) carboxylates proceeds, in conformity with mechanism (3), via two pathways, depending on the structure of the ligand[60]. The formation of carboxymethyl radicals is the preferred pathway (98 to 100%) for MTA. In the reaction involving manganese(III) propionate the alternative pathway involving decomposition with formation of $CH_3\dot{C}H_2$ makes a contribution of ~6%, while the thermolysis of phenylacetate proceeds almost exclusively via this pathway [see mechanism (3)].[60] Thus, on oxidation with MTA in acetic acid (110 °C), benzene and chlorobenzene give rise to mixtures of the corresponding phenylacetic acids, benzyl acetates, benzylidene acetates, and benzaldehydes, while toluene gives rise to methylbenzyl acetate (67%), benzyl acetate (10%), benzaldehyde (3%), and traces of bibenzyl[61]. Acetoxymethylation products also arise from the oxidation at 100 °C of anisole[60,62], dimethoxybenzenes[61], and 2-methylnaphthalene[60].

The thermolysis of MTA (including electrolytically generated MTA[63]) in acetic acid can also be used for the introduction into the aromatic substrate molecule of other radicals generated via the mechanism

$$RH + \dot{C}H_2CO_2H \rightarrow R^{\cdot} + AcOH \quad .$$

For example, the nitromethylation ($R = CH_2NO_2$) [63,64] and acetylmethylation ($R = CH_3COCH_2$) [65] of toluene and substituted benzenes have been achieved in this way.

It is of interest that the oxidation of methylferrocene with MTA in acetic acid does not yield acetoxymethylation products, but leads to a mixture of diarylmethanes[66]:

$$AcOH \xrightarrow{MTA} \dot{C}H_2CO_2H \xrightarrow{RCH_3} RCH_2^{\cdot} \xrightarrow{MTA} RCH_2^{+} \xrightarrow{RCH_3} RCH_2R' \quad ,$$

where R = ferrocenyl and R′ = 2-methylferrocenyl, 3-methylferrocenyl, or 3′-methylferrocenyl.

In the oxidation of substrates with fairly low ionisation potentials (<8 eV) an electron transfer process competes with radical substitution. Thus 1- and 2-methoxynaphthalenes are acetoxylated in the ring at 100 °C,[67] while *p*-methoxytoluene yields mainly *p*-methoxybenzyl acetate[59,60]. The selectivity of the reaction can therefore be regulated by suppressing or activating one of these processes.

The thermolysis of MTA in acetic acid (140 °C) is accelerated by a factor of 3–4 when potassium acetate is added[62] and also increases appreciably when acetic anhydride is added to the reaction mixture[68] or anhydrous MTA is used[60,68]. The relative yield of the acetoxymethylation product also increases following the addition of manganese(II), which retards the electron transfer reaction, as in the case of cobalt(III) (see above)[60].

On the other hand, radical processes are fully suppressed in the presence of strong acids, which makes it possible to reduce the reaction temperature to 20–40 °C.[36] The products of the oxidation of alkylarenes under these conditions are, as for cobalt(III), benzyl acetates in an inert atmosphere and carboxy-compounds in the presence of oxygen.

The oxidation of alkylbenzenes in boiling acetic acid in the presence of H_2SO_4, CF_3SO_3H, and particularly $HClO_4$ leads to the formation of diarylmethanes in high yields[45]. Under these conditions, the effect of MTA is analogous to those of CTA (see above) and the iron(III) perchlorate normally employed in this reaction (see below), differing, however, by a greater selectivity (the amount of disproportionation and polymerisation products is in this instance minimal), which makes the process synthetically valuable.

In contrast to alkylbenzenes, *p*-methoxytoluene yields under these conditions biaryls, but in the presence of weaker acids (CCl_3CO_2H, CF_3CO_2H) or at lower $HClO_4$ concentrations the main products become diarylmethanes[42]. It is of interest that in the analogous reaction with $Fe(OAc)_3$ only diarylmethanes are formed in both cases. The different behaviour of manganese(III) and iron(III) acetates has been explained[42] by the different stabilities of the trinuclear clusters of the type $[M_3O(OAc)_6L_3]OAc$ (L = AcOH for manganese and H_2O for iron), which act as bases in the reaction involving the elimination of a proton from the radical-cation (see above).

Manganese(III) trifluoroacetate reacts with mesitylene[48,49] and durene[49] in TFAA with formation of mixtures of dehydrodimers [see mechanisms (7)–(10)], but, in contrast to cobalt(III) (again see above), mainly diarylmethanes are formed in this instance and the reactivities of MTA and $Mn(OCOCF_3)_3$ solutions in TFAA are virtually identical[48].

Manganese(III) sulphate oxidises the methyl group in 1-methylnaphthalene, giving rise to the corresponding aldehyde and 1,4-naphthoquinone, but in the case of 2-methylnaphthalene the oxidation does not involve the methyl group and the reaction products are only 2- and 6-methyl-1,4-naphthoquinones[69].

The oxidation of 1-bromonaphthalene under these conditions is accompanied by a 1,2-shift to the substituent and the formation of 2-bromo-1,4-naphthoquinone, as in the oxidation with cerium ammonium sulphate (see below).

Like CoF_3, manganese(III) fluoride oxidises benzene to a mixture of cyclic polyfluoro-derivatives[18], but it acts more selectively and yields mainly polyfluorocyclohexenes.

4. Cerium(IV)

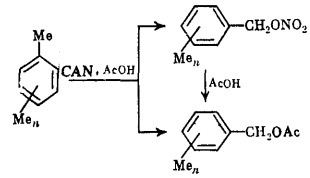
The first data on the oxidation of substituted toluenes to benzaldehydes by cerium dioxide in H_2SO_4 were obtained at the beginning of this century[70,71], but the yields of these reactions were not indicated and the yield of benzaldehyde in the oxidation of toluene by electrolytically generated cerium(IV) sulphate, described much later[72], amounted to only 8%.

Systematic studies of the oxidation of alkyl derivatives of aromatic compounds by cerium(IV) salts probably began towards 1965 when the quantitative oxidation of benzyl alcohols to benzaldehydes by cerium ammonium nitrate (CAN) in 50% acetic acid solution was described[73]. It was later shown[74] that under these conditions benzaldehydes are the main products of the oxidation of toluenes (benzyl alcohols and benzyl acetates are formed simultaneously). The yield of benzaldehydes increases on passing from toluene to *p*-xylene from 36 to 73%, but the introduction of stronger electron-donating substituents (OH, NH_2, or OMe) leads to the charring of the reaction mixture. Electron-accepting substituents lower the overall yield of oxidation products and in the case of *p*-chlorotoluene a simultaneous increase of the fraction of *p*-chlorophenylmethanol was observed[73]. In 100% acetic acid the main reaction products are benzyl acetates, whose yield also falls on passing to *p*-halogenotoluenes with a simultaneous increase of the fraction of carbinols and aldehydes in the reaction products; *p*-nitrotoluene is not oxidised at all under these conditions, but the replacement of acetic acid by 6 *N* $HClO_4$ or 3.5 *N* HNO_3 makes it possible to oxidise to aldehydes even chloro- and nitro-toluenes (with yields up to 75 and 50% respectively)[74,75]. Under the same conditions, toluene and mesitylene give rise to monoaldehydes in a quantitative yield, while ethylbenzene and diphenylmethane are oxidised to acetophenone and benzophenone with yields of 78 and 76% respectively[75]. The quantitative synthesis of anisaldehyde in 90% acetic acid from *p*-methylanisole, which completely charred in 50 and 100% acetic acid according to Trachanovsky and Young[74], has also been described[75].

The reactivity in the oxidation by CAN in aqueous acetic acid solutions decreases in the sequence *p*-xylene > *m*-xylene > *o*-xylene > toluene[76]. The reaction is accelerated in the presence of HNO_3 and is retarded by the addition of AcO^-, the rate of oxidation being a maximum in ~85% of acetic acid in all cases. The activating effect of HNO_3 is attributed[76] to the formation of the cation $Ce(NO_3)_2^{2+}$, but the inhibiting effect of added AcO^- is believed to be due to a decrease of oxidising activity when the ligands in the hexanitratocerate(IV) anion are exchanged for acetate ions[76].

The kinetics of the oxidation of toluene[77,78], xylenes[78], and nitro- and chloro-toluenes[76] by cerium(IV) in an AcOH–$HClO_4$ mixture are described by a second-order equation and the reaction mechanism is said to include[77,78] electron transfer and the formation of a benzyl-type radical as the rate-limiting stage. However, it is of interest that *p*-chlorotoluene is oxidised faster than toluene under these conditions; this has been explained[77] by the "specific features of the resonance interaction". The primary and main products of the oxidation of substituted toluenes by CAN are benzyl nitrates, which can be isolated in a fairly satisfactory yield when the reaction is carried out in hydrocarbon solvents, but in reactions in aqueous acids they are rapidly hydrolysed to carbinols, which are subsequently oxidised to aldehydes[79]. In the case of *o*-xylene the nitrate/aldehyde ratio varies from 1.5 to 4, the yield and ratio of the products depending on the rate of addition of the CAN solution, the nature of the acid (HNO_3, H_2SO_4, or AcOH), and the presence of an aliphatic hydrocarbon solvent. It is believed[79] that the reaction involves the formation of a cyclic transition state with a dimeric cerium(IV) complex, leading to nitrates and carbinols as a result of the transfer of two electrons and a proton. In the case of toluene and *p*-xylene, containing a sterically unshielded methyl group, the nitrates formed are more labile and both reactions terminate with formation of an aldehyde.

The oxidation of polymethylbenzenes (mesitylene, isodurene, hemimellitol and hexamethylbenzene) by CAN in acetic acid is described by a similar mechanism[80]:



The required stoichiometric ratio CAN/substrate = 2 decreases in the presence of oxygen. The nitrate/acetate ratio depends on the reaction time and the rate of solvolysis of the nitrate and varies from 1.5 for mesitylene to 5 for hemimellitol, increasing with increase of the fraction of undissolved CAN under heterogeneous conditions and being virtually independent of the structure of the substrate in the presence of NH_4NO_3 in the reaction mixture.

The proportions of the products in the case of isodurene and hemimellitol show that the oxidation involves mainly the 2-methyl group, which confirms the formation of a substrate radical-cation (the radical substitution takes place mainly in the 5-position[81]). The benzyl radical formed in the second stage of the reaction is oxidised further, according to the data of Baciocchi et al.[80], but not via carbonium ion [mechanism (6)]; it results from ligand transfer and proceeds via an intermediate with a Ce(IV)–CH_2Ar linkage, undergoing subsequently competitive oxidative solvolysis with formation of the acetate or with oxidative substitution yielding the nitrate#.

According to Eberson and Oberrauch[82], the anodic oxidation of isodurene in the AcOH–Bu_4NNO_3 mixture and the reaction of isodurene with CAN give virtually identical results, but the authors[82] suggest that the first stage in the

#For further details about the mechanism of oxidative substitution and solvolysis, see C.L.Jenkins and J.K.Kochi, J.Amer.Chem.Soc., 92, 856 (1972).

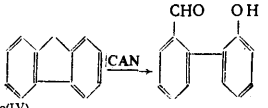
reaction with CAN involves the transfer of an α-hydrogen from the substrate molecule via mechanism (2*a*) (X = NO_3).

Among all the polymethylbenzenes, only mesitylene undergoes ring acetoxylation apart from benzyl oxidation, the yield of 2,4,6-trimethylphenyl acetate amounting to 50% of the beginning of the reaction and falling to 25% towards its end[78] (however, one should note that the oxidation of mesitylene by CAN in acetonitrile gives rise only to 3,5-dimethylbenzyl nitrate[83]). The formation of a "ring" acetate in the case of mesitylene is consistent with data for the oxidation of methylbenzenes by cerium(IV) trifluoroacetate in the presence of $LiOCOCF_3$, which leads to the preferential formation of biaryls (X) (40%) [together with diarylmethanes (VII) (10%) and benzyl trifluoroacetate (~1%)—see mechanisms (6)–(10)][84], the ratio (X) : (VII) falling with increase of reaction temperature and with increase of the $LiOCOCF_3$ concentration. Under these conditions, benzene is oxidised with difficulty (8% of phenyl trifluoroacetate and 1% of biphenyl are formed), toluene gives rise only to a mixture of phenyltolylmethanes (15%) and benzyl trifluoroacetate (15%), *p*-xylene yields methylbenzyl trifluoroacetate (8%) and diarylmethanes (10%), while durene is converted into biduryl (2%) and diarylmethanes (97%).[84]

Another example of ring acetoxylation is the oxidation of anisole by CAN in acetic acid (40 °C, N_2),[85] which leads to a mixture of *o*- and *p*-acetoxyanisoles (*o*/*p* = 0.82). The reaction is of first order with respect to PhOMe and CAN and of the reciprocal order with respect to cerium(III); it is greatly accelerated by the addition of ammonium nitrate. The reaction products do not contain nitrates and the proportions of the isomeric acetates are consistent with the distribution of electron density in the anisole radical-cation [the EPR spectra of the aromatic radical-cations obtained by oxidation with cerium(IV) salts have been described[86]]. The reactions have mechanism (8) (see above).

In 90% trifluoroacetic acid in the presence of alkali metal chlorides and bromides CAN reacts fairly readily with *p*-toluic acid to form products of the oxidative halogenation of the aromatic ring—3-halogeno-4-methylbenzoic acids[54]. It has been suggested that the occurrence of a reaction via mechanism (8) is facilitated in this instance by the formation of cerium(IV) complexes containing ligands in steric proximity—halides and 4-methylbenzoate ions[54]. It is of interest that, with increase of the water content in the reaction system, the yield of ring halogenation products falls owing to the formation of the corresponding benzyl halides, which is associated, according to the authors[54], with the displacement of arenecarboxylate ligands from the inner coordination sphere of the oxidant by water.

In the oxidation of 1,2-diarylethanes by CAN in 70% aqueous acetonitrile[87] the first stage also involves the formation of a radical-cation, which decomposes into a benzyl radical and a benzyl cation, leading to benzaldehydes, benzyl nitrates, and benzyl alcohols. The rate of reaction increases after the introduction of electron-donating substituents into the aromatic ring and falls when electron-accepting substituents are introduced. The oxidation of fluorene[88] and aryl triarylmethyl ketones by CAN in acetic acid also involves the oxidative cleavage mechanism[89]:



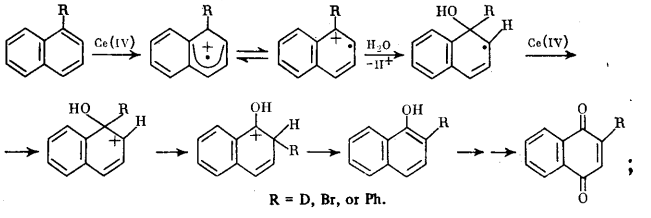
$$Ar_3CCOAr' \xrightarrow[-2Ce(III)]{2Ce(IV)} Ar_3C^+ + Ar'CO^+ \rightarrow Ar_3COH + Ar'CO_2H \ .$$

In the first stage of its oxidation with CAN in methanol or acetic acid[90], anthracene gives rise to 9-anthryl nitrate, whose reaction with the anthracene radical-cation produces 9-anthryl nitrite and the anthrol radical, which is then converted into bisanthrone or is oxidised by CAN to 10-acetoxy- and 10-methoxy-anthrols and also to anthraquinone (via 9,10-dihydro-10-oxo-9-anthryl nitrate). On the other hand, it has been shown[91] that the analogous reaction in acetonitrile gives rise to a 3 : 1 mixture of anthraquinone and 9-nitroanthracene. Ring nitration products are formed under these conditions also from benzene, nitrobenzene, toluene, and naphthalene.

The oxidising properties of CAN can be used successfully also in reactions of alkylarenes with acyl peroxides, for example, via the mechanism[92]

$$(iso\text{-}PrCO_2)_2 + 2[Ce(NO_3)_6](NH_4)_2 + PhMe \rightarrow o\text{-}MeC_6H_4Pr\text{-}iso + 2Ce(NO_3)_3 + 4NH_4NO_3 + 2HNO_3 \ .$$

An interesting reaction (a 1,2-shift of the substituent) has been discovered in the study of the oxidation of 1-substituted naphthalene by cerium ammonium sulphate[93]. The anodic oxidation of the same substrates proceeds analogously[94]:



R = D, Br, or Ph.

Cerium pyridinium chloride $(C_5H_5N)_2CeCl_6$ (CPC) has been used to oxidise polymethylbenzenes in methanol and ethanol[95]. In the case the oxidant consists of the products Ce(IV) $(Cl)_x(RO)_y$ of the ligand exchange between CPC and the solvent, which exhibit different reactivities depending on R. The rate of the oxidation and "spontaneous" reduction of CPC in methanol is higher by two orders of magnitude than in ethanol. In the absence of oxygen, the reaction products are the corresponding benzyl chlorides and alkoxymethylbenzenes, the latter becoming the sole reaction product after more prolonged refluxing of the reaction mixture, which makes this process valuable from the synthetic point of view. It is of interest that, in contrast to hexamethylbenzene and durene, which give satisfactory yields of products, mesitylene is almost inert with respect to oxidation under these conditions.

The ratio of the chloro- and methoxy-derivatives in the oxidation of durene by CPC in methanol remains constant during the reaction, increasing after the addition of LiCl, but under these conditions methoxylation is not fully suppressed, which confirms the ligand transfer mechanism in the benzyl radical oxidation stage proposed by the author[95] (see above). In the reaction in the presence of oxygen, the dimethylacetate of 2,4,5-trimethylbenzaldehyde is formed from durene, but hydrolyses during isolation (the yield of aldehyde is 65%). It is of interest that the oxidation of Cl^- to Cl_2, which takes place with difficulty in alcohols, occurs readily when CPC is refluxed in acetonitrile.

Like cobalt(III) and manganese(III) fluorides (see above), cerium tetrafluoride is used to synthesise cyclic polyfluoro-derivatives from benzene (250–480 °C). However, this results in a mixture containing polyfluorobenzenes, polyfluorocyclohexenes, and polyfluorocyclohexadienes[18,96].

Cerium tetra-acetate reacts with toluene in acetic acid (110 °C) via the general mechanism (3) and give rise to three products: (I)–(III).[97] The thermolysis of $Ce(OAc)_4$ in acetic acid takes place in the same way as for $Mn(OAc)_3$

with formation of carboxymethyl radicals, but, in contrast to manganese(III), the acetoxymethylation is in this case suppressed by the addition of acetic anhydride and potassium acetate. The reaction with benzene and chlorobenzene yields only arylacetic acids (41 and 36%). The authors suggest[97] that the role of acetic anhydride consists in binding the acids produced into mixed anhydrides, which are resistant to oxidation.

It is of interest that the photolysis of $Ce(OAc)_4$ is accompanied by decarboxylation and the formation of methyl radicals [see mechanism (3)].[97]

5. Iron(III)

Potassium hexacyanoferrate(III) $K_3Fe(CN)_6$ and iron(III) chloride $FeCl_3$ are most frequently used as oxidants. The hexacyanoferrate(III) is normally employed in aqueous solutions and, being a weak oxidant, is capable of oxidising only aromatic compounds with a fairly low ionisation potential (such as methylphenols[98,99] and alkoxybenzenes[99]), giving rise thereby to substituted biphenyls.

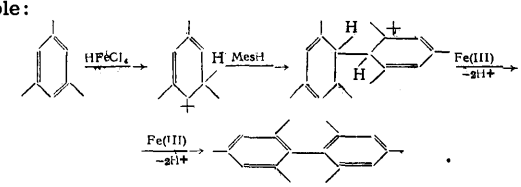
Under alkaline conditions (DMSO–H_2O–OH^-), substituted toluenes containing powerful electron-accepting groups (NO_2 or Me_3N^+) can also be oxidised as a result of the formation of benzyl anions:

$$ArCH_3 \xrightarrow[DMSO]{OH^-} ArCH_2^- \xrightarrow{Fe(III)} ArCH_2^{\cdot} \xrightarrow{Fe(III),\ H_2O} ArCH_2OH \ .$$

The rate of reaction increases with increase of the DMSO content in the solvent and after the introduction of halide ions (Cl > Br > I).[100]

In contrast to the hexacyanoferrate(III), anhydrous iron(III) chloride is a fairly powerful oxidant and interacts with aromatic compounds to form chlorination and dehydrodimerisation products. These reactions have been known since the end of the last century and have been discussed in fair detail in reviews[101,102]. It is noteworthy that interest in reactions of this type has not flagged. Thus conditions have been found for the polychlorination of benzene with iron(III) chloride in a melt with NaCl in the presence and absence of O_2.[103] The oxidative coupling of alkylarenes by iron(III) salts is being particularly vigorously investigated[49,104–107].

The mechanism of the formation of biaryls proposed by Kovacic and coworkers[102] presupposes the protonation of the substrate by the HCl–$FeCl_3$ complex and further transformations of the type of cationic polymerisation, for example:



The reactivity of polymethylbenzenes should thus be determined by their basicity, but it has been shown[104–106] that the ionisation potential of the substrate is of decisive importance in these reactions and the formation of biaryls and diarylmethanes under the influence of $FeCl_3$ has much in common with anodic oxidation and includes therefore electron transfer [mechanism (1)] and electrophilic attack on the substrate via mechanisms (7), (9), and (10).

The oxidation of polymethylbenzenes by iron(III) chloride leads to the formation of diarylmethanes in all cases, except for *m*-xylene and mesitylene[49,103–106]. A detailed study of the oxidation of mixtures of methylbenzenes under these conditions showed that radicals of the benzyl type and hence diarylmethanes [see mechanism (6)] are formed from radical-cations with a high charge density in the substituted position of the aromatic ring (for example, in the case of durene). Accordingly, durene in mixtures with benzene, *p*-xylene, toluene, and mesitylene yields only diarylmethanes[103], while the analogous reaction of naphthalene can serve as a preparative method for the synthesis of 1-arylnaphthalenes[105]. The yield of products in the latter case depends on the nucleophilic properties of the alkylarene relative to the naphthalene radical-cation.

It is of interest that even durene and xylene give rise to ring-chlorinated compounds only as side products on treatment with $FeCl_3$.[49,102] Only mesitylene is appreciably chlorinated in the ring under these conditions[49]. The yield of chloromesitylene decreases with increase of the reaction temperature and in the presence of water and also increases with increase of the $FeCl_3$ mesitylene ratio. Chlorination thus probably proceeds via ligand transfer in the complex of $FeCl_3$ with the substrate radical-cation and not via mechanism (5).[49] The reactions under the influence of copper(II) halides takes place similarly (see below).

The oxidation of methylbenzenes by various iron(III) salts (chloride, nitrate, sulphate, acetate, and perchlorate) in boiling acetic acid in the presence of $HClO_4$ also leads to the selective synthesis of diarylmethanes[45,106]. It is of interest that the yield of diarylmethanes increases in the sequence PhPr-iso << PhEt < *p*-ClC_6H_4Me, while in the reactions of $FeCl_3$ with the same substrates in the absence of a solvent the opposite sequence obtains: PhMe < *p*-ClC_6H_4Me < PhEt < PhPr-iso.[101] The catalytic nature of the reaction in relation to the iron(III) salt in the presence of $HClO_4$, noted in many instances[105], has been shown[107] to be caused by the oxidation by perchloric acid of the $FeCl_2$ produced, so that the synthesis of diarylmethanes can be carried out in the $FeCl_2$–$HClO_4$ system[107].

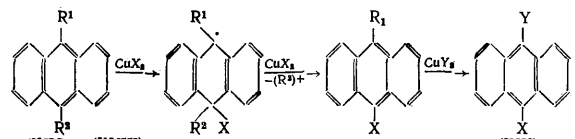
6. Copper(II) §

Copper(II) halides are usually employed as halogenating agents under both heterogeneous[107–117] and homogeneous[117–126] conditions. The photolysis of $CuCl_2$ in toluene affords benzyl chloride (86%) via the mechanism

$$PhCH_3 + Cl^{\cdot} \rightarrow PhCH_2^{\cdot} \xrightarrow{CuCl_2} PhCH_2Cl + CuCl \ .$$

Small amounts (0.5%) of chlorotoluenes and bibenzyl are formed at the same time[108].

The heterogeneous reactions of copper(II) salts usually involve the oxidation of a radical intermediate formed as a result of ligand transfer in the first stage [mechanism (2)]. The halogenation of anthracene and 9-substituted and 9,10-disubstituted anthracenes (XIV)–(XVIII) in non-polar solvents (PhCl, CCl_4, etc.) takes place in this way[109,110]:



(14)

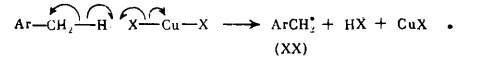
(XIV) – (XVIII) (XIX)

X,Y = Cl or Br

(XIV) a) R^1 = X, Y, Alk or Ar; R^2 = H; b) R^1 = X or Y; R^2 = Alk or Ar;
(XV) a) R^1 = OAlk or COAlk; R^2 = H; b) R^1 = H, R^2 = COAlk;
(XVI) R^1 = Alk or Ar; R^2 = Ar, Et or CH_2Ph;
(XVII) R^1 = Ar, Et, CH_2Ph, X or Y; R^2 = Me;
(XVIII) a) R^1 = OAlk or COAlk; R^2 = Me; b) R^1 = OAlk or OCOAlk; R^2 = H, Ph, Et or CH_2Ph.

§ The use of copper(III) complexes of oxidants has been described only for ascorbic acid and catechol [see Y.Yano, S.Takano, V.Kato, and W.Tagaki, J.Chem.Soc., Perkin Trans.II, 1227 (1979)].

According to mechanism (14), these reactions are accompanied by "transhalogenation" or substitution of hydrocarbon [compounds (XVI) [111,112]] or acyl [compounds (XVb) [113]] groups by the halogen. 9-Methylanthracene also reacts via mechanism (14),[109] but 10-substituted 9-methylanthracenes (XVII) and (XVIIIa) form under these conditions radicals of the benzyl type in the first stage[111,112] via the mechanism



(XX)

In the case of substrates (XVII) the radical (XX) is oxidised further via mechanism (5) to a halogenomethyl derivative $ArCH_2X$. More stable radicals containing an acyl or alkoxy-group [compounds (XVIIIa)] dimerise to the corresponding diarylethanes under these conditions via mechanism (6).[114]

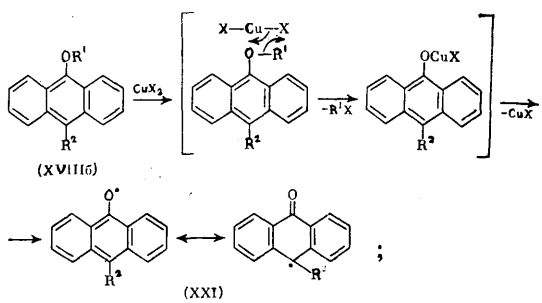
In the case of 9-alkoxy- (particularly methoxy) and 9-acyloxy-anthracenes (XVIIIb) there is also a possibility of the mechanism invclving the "radicalisation" of the substrate[115].

Depending on the substituents in the 10-position, the radical (XXI) dimerises further to bianthronyl (XXII), is halogenated to halogenoanthrone (XXIII), or gives rise to quinomethides (XXIV).[115]

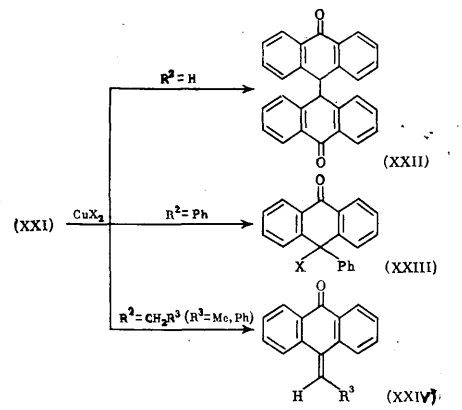
The reaction between $CuBr_2$ and 2-benzyloxynaphthalene proceeds analogously to reaction (15).[116] The product is a mixture of 2-benzyloxy-1-bromonaphthalene (17%), 1-bromo-2-naphthol (61%), di-β-naphthol (1.4%), and benzyl bromide (10%). It is of interest that $CuCl_2$ yields only products of the chlorination in the 1-position under these conditions. The reaction of $CuBr_2$ with 2-ethoxy- or 2-methoxy-naphthalene takes place in the same way[116]. The halogenation of pyrene, perylene, and tetracene by anhydrous copper(II) halides in non-polar solvents has also been described[117,118]. It has been suggested[116] that the reaction proceeds as homolytic decomposition of a π-complex of $CuCl_2$ with a substrate molecule. It is of interest that the oxidation proceeds in this instance in PhCl but not in CCl_4.[118]

Under homogeneous conditions, the CuX_2 molecule is as a rule solvated and cannot participate in the ligand transfer. In this case the mechanism involving electron transfer becomes more probable [mechanism (1)].

Thus, on treatment with CuX_2 (X = Cl or Br) in MeOH, 9-alkyl- and 9-aryl- anthracenes are converted by successive three-stage oxidation via mechanisms (1) and (8) into 10-alkyl and 10-aryl-10-methoxyanthrones (XXV).[119] As in other cases, when a methyl group is present, a benzyl-type radical is also formed from the substrate radical-cation and is converted via mechanisms (5) and (6) into methoxymethyl derivatives and diarylethanes (XXVII) (see above).



(XVIIIб) (XXI) (15)

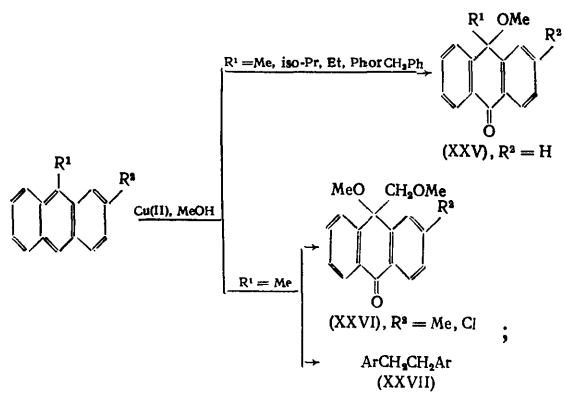


(XXI) (XXII) (XXIII) (XXIV)

It is of interest that the products of type (XXVI) and (XXVII) are not formed in the presence of a substituted methyl group R^1, which is believed[119] to be due to steric factors, preventing the stabilisation of the radical ArĊHR.

Under homogeneous conditions, copper(II) bromide brominates 3,4,5-trimethylanisole in the ring[120]. Alkylbenzenes react similarly with anhydrous $CuBr_2$, but in the presence of even small amounts of water the main products are diarylmethanes (benzyl bromides are also formed in smaller amounts). Mesitylene gives rise to only bromomesitylene in both cases[121].

The heterogeneous oxidation of toluene, *p*-xylene, and mesitylene with copper(II) chlorides also proceeds via a radical-cation formation stage according to Cummings and Milner[122] and leads to the formation of diarylmethanes and ring-chlorination products in conformity with mechanisms (7) and (8), the yield of the latter increasing with increase of the stability of the radical-cation and amounting to 20% for $C_6H_4Me_2$ and 90% for $C_6H_3Me_3$.



(XXV), $R^3 = H$; (XXVI), $R^3 = Me, Cl$; $ArCH_2CH_2Ar$ (XXVII)

$Ar = C_{14}H_9$, 2-$MeC_{14}H_8$ or 2-$ClC_{14}H_8$.

The yield of diarylmethanes decreases correspondingly from 90% for C_6H_5Me to 80% for $C_6H_4Me_2$. Diarylmethanes are formed exclusively when *p*-xylene is refluxed with $Cu(OAc)_2$ in acetic acid containing $HClO_4$.[45]

The ability of $CuCl_2$ to react via the ligand transfer mechanism [mechanism (2*b*)] has been used to oxidise the radical-cations generated by other oxidants[123]. The reaction of methylbenzenes with the peroxydisulphate anion in aqueous acetonitrile in the presence of $CuCl_2$ yields exclusively ring-chlorination products[123], while the pathway followed in the reaction of Cl^- with the corresponding radical-cations depends on the stability of the latter and the contributions of α-chlorination in the sequence mesitylene < *m*-xylene < *p*-xylene ≅ toluene are 25, 90, 100, and 100% respectively[123].

On the other hand, in the reaction of methylbenzenes with peroxydisulphate in acetic acid containing 9% of TFAA, the introduction of copper(II) acetate suppresses ring acetoxylation and promotes the formation of substituted benzyl acetates and trifluoroacetates. In the case of mesitylene the relative yield of the corresponding product is 92% [33% in the absence of copper(II)].[124]

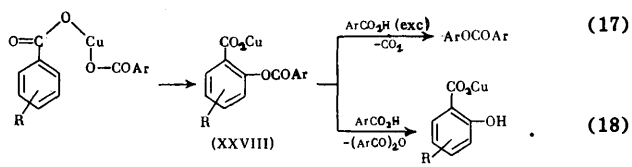
In conformity with the electron transfer mechanism, the oxidation of *p*-cymene in the $AcOH-S_2O_8^{2-}-Cu(OAc)_2$ system leads to isopropylbenzyl acetate[125]. The oxidation of the radical intermediate by copper(II) via mechanism (8) plays an important role in the acetoxylation of naphthalene under the same conditions. In the absence of copper(II) the reaction does not occur and the replacement of copper(II) by iron(III) leads to the formation of methyl- and acetoxymethyl-naphthalenes[125].

Copper(II) carboxylates introduce the acyloxy-group into the rings of alkyl derivatives of aromatic substrates via the following mechanism[126,127]:

$$2(R^1CO_2)_2Cu + PhR^2 \rightarrow R^2C_6H_4OCOR^1 + 2R^1CO_2Cu + R^1CO_2H \quad (16)$$

The yield of acyloxy-derivatives increases in the presence of copper(II) oxide, reacting with the liberated acid and (or) oxygen, which regenerates the copper(II) salt[127,128].

Substituted copper(II) benzoates can also be oxidised by an intramolecular mechanism with formation of *o*-benzyloxybenzoates (XXVIII):[128]



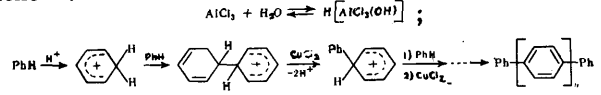
(17)

(18)

In the presence of water and an excess of acid, compound (XXVIII) is decarboxylated [mechanism (17)] with formation of the corresponding phenol after hydrolysis. Thus *o*- and *p*-toluic acids yield *m*-cresol under these conditions and *m*-toluic acid gives rise to a mixture of *o*- and *p*-cresols[126]. The thermolysis of copper(II) benzoate in benzoic acid produces phenyl benzoate, whose yield can be increased in the presence of oxygen, which regenerates copper(II). This reaction constitutes the basis of an industrial method for the synthesis of phenol from toluene via benzoic acid[126-128]. In aprotic media (Ph_2O, Ph_2CH_3, cyclohexane, etc.) the decarboxylation is suppressed and the reaction of compound (XXVIII) with the liberated acid molecule leads to the formation of salicylates [mechanism (18)].[126]

The interactions of alkylbenzenes (and also benzene, anisole, and diphenyl ether) with copper(II) benzoates usually yield the products of all three reactions. Thus in the case of toluene 51, 16, and 33% of the products correspond to the contributions of reactions (16), (17), and (18) respectively[126].

An interesting variant of the utilisation of the oxidising capacity of copper(II) is the application of $CuCl_2$ in combination with $AlCl_3$ for the cationic polymerisation of benzene[129]:

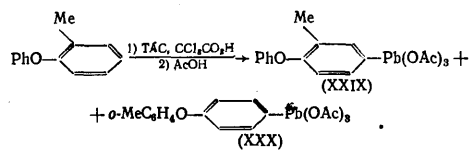


7. Lead(IV)

The reactions of aromatic compounds with lead(IV) salts include three main types of transformations depending on the type of substrate, nature of the ligands, and the conditions of synthesis: (a) the substitution of lead (plumbation) in the aromatic ring via S_E-type reactions, leading to the formation of aryl lead(IV) tricarboxylate[130-142], which then decomposes via heterolytic[138-142] or homolytic[130-137] mechanisms; (b) radical substitution via mechanism (3) under the conditions of thermal[128,143-154], photochemical[143-145], or radical-initiated[147] decomposition of lead(IV) carboxylates; (c) electron transfer from the substrate molecule via mechanism (1) with subsequent transformations of the radical-cation via mechanisms (5)–(10).[45,49,140,141,147]

Plumbation is usually less important in the reactions of lead(IV) carboxylates than, for example the substitution of thallium (thallation) in the case of thallium(III) (see below), but the contribution of this reaction becomes appreciable with increasing nucleophilicity of the aromatic ring in the presence of strong electron-donating substituents. Anisole and dimethoxybenzenes[130-133] are plumbated even on treatment with lead tetra-acetate (LTA) in acetic acid at 80 °C. Acetoxylation via a one-electron transfer mechanism with formation of a radical-cation [mechanisms (1) and (8)] and giving rise to acetoxyanisoles in the case of anisole (*o*/*p* = 35/65) is a competing reaction under these conditions. *m*-Dimethoxybenzene, which is the most reactive in plumbation reactions, exhibits the smallest tendency towards acetoxylation under these conditions[133]. The role of plumbation increases also with the increase of the electrophilicity of the lead(IV) atom as a result of the addition of strong acids. The replacement of acetic acid by halogenoacetic acids leads to the formation of lead(IV) halogenoacetates, giving rise to plumbation products even at room temperature[134-137]. The plumbation of 2,4-dimethoxybenzene by lead(IV) monohalogenoacetates leads to the trishalogenoacetates $ArPb(OCOCH_2X)_3$ (X = Cl, Br, or I) in yields of 94–99%.[134] The reaction with aromatic ethers PhOR (R = Me, Et, n-Bu, or Ph) proceeds similarly, but, when they are isolated from reaction mixture, hydrolysis products are formed—the oligomers of plumboxanes $\{[ArPb(OCOR)_2]_2O_2\}_m$, which readily form aryl-lead triacetates on treatment with acetic acid[134-137].

An increase of the number of halogen atoms in halogenoacetic acids makes possible direct plumbation of *o*-halogeno-substituted (F, Cl, Br, or I) anisoles and phenetoles, derivatives of diphenyl ether, alkylbenzenes, biphenyl, benzene, and halogenobenzenes[137]. It is of interest that the oxidation of iodobenzene with LTA in trichloroacetic acid yields iodosobenzene diacetate $PhI(OAc)_2$ (after treating the reaction mixture with acetic acid) and not the plumbation product[137]. The plumbation reactions involving substituted benzenes are highly selective and lead almost exclusively to *p*-derivatives. Monosubstituted diphenyl ethers are usually plumbated in the *p*-position of the unsubstituted ring. Only in the case of 2-methyl-1-phenoxybenzene were two products obtained [(XXIX)/(XXX) = 7/3]:[137]



The high selectivity of the plumbation reaction has been explained[137] by the increased reactivity of the *m*- and *o*-isomers in the protodeplumbation reaction under the influence of the acid in the reaction mixture, although this explanation is inconsistent with the reactivity sequence of other organometallic compounds in the protodemetallation reaction[146]. When the substrate is highly nucleophilic, the $ArPbX_3$ formed can react as an electrophile and can give rise to the products Ar_2PbX_2 or $ArAr'PbX_2$.[137]

On treatment with TFAA, aryl-lead tricarboxylates decompose rapidly with formation of aryl trifluoroacetates or (in the presence of aromatic substrates) biaryls via the mechanism[138,139]:

$$ArPb(OCOCF_3)_3 \underset{HOCOCF_3}{\overset{H^+}{\rightleftharpoons}} Ar\overset{+}{P}b(OCOCF_3)_2 \xrightarrow{-Pb(OCOCF_3)_2} Ar^+ \begin{cases} \xrightarrow[-H^+]{Ar'H} ArAr' \\ \xrightarrow[-H^+]{TFAA} ArOCOCF_3 \end{cases}$$

The rate of decomposition of aryl-lead tristrifluoroacetates is proportional to the relative stability of the aryl cations formed, so that the derivative of *m*-nitrophenyl-lead is most resistant to the action of TFAA.[138] It is of interest that the rate of formation of biaryls under these conditions is higher than the rate of trifluoroacetoxylation; this has been explained[139] by the preliminary formation of a π-complex between the hydrocarbon molecule and the species in which the Ar–Pb band is still preserved. The yield of biaryl increases with increase of the number of electron-donating substituents in the substrate ring.

It is noteworthy that the oxidation of xylenes, durene, mesitylene, and hexamethylbenzene by lead(IV) trifluoroacetate in the TFAA–CH_2Cl_2 system yields, apart from biaryls, also diarylmethanes (together with products of acetoxylation in the ring and in the side chain), i.e. the process also includes an electron transfer stage and the formation of radical-cations [see mechanisms (1), (7), and (9) [49,140,141]]. The oxidation of toluene with lead tetraacetate in TFAA produced after hydrolysis a mixture of cresols (28%),[140–142] bitolyls (4.5%), and *p*-tolylphenylmethane (0.6%), the yield of bitolyls increasing with increase of the ratio TFAA/LTA.[140,141]

In the absence of strong acids, the reactions of alkylarenes with LTA in acetic acid at 80 °C lead exclusively to α-acetoxylation products[132,149–152]:

$$R^1\text{—}C_6H_4\text{—}CH_2R^2 \rightarrow R^1\text{—}C_6H_4\text{—}CHR^2OAc\ ;$$

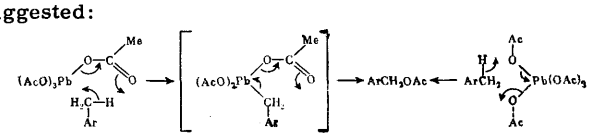
R^1 = H, OMe, Me, t-Bu, Br, or NO_2; R^2 = H or Me.

Di- and tri-phenylmethanes, fluorene, and hexamethylbenzene react similarly. According to Radhakrishnamurti and Mohapato[152], the reaction kinetics are described by the equation

$$-\frac{d[Pb(IV)]}{dt} = k[ArH]^n[Pb(IV)],$$

where $n = 2$ for substituted toluenes (R^1 = H, OMe, or Me and R^2 = H) and $n = 1$ for Ph_2CH_2, Ph_3CH, and fluorene. The rate of reaction remains unchanged in the presence of small amounts of H_2O (5% in acetic acid) and increases when acetic acid is replaced by propionic acid and also in the presence of Cl^-, Mn^{2+}, and dimethylformamide (DMF). The addition of other solvents inhibits the reaction: Me_2SO > MeCN ≅ cyclohexane > CH_2Cl_2 > $PhNO_2$ > PhH.[152]

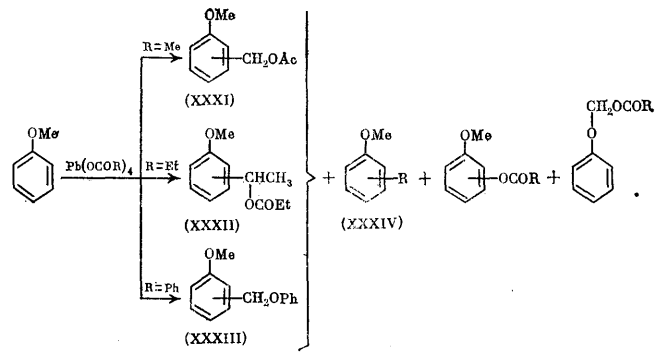
The detailed mechanism of this reaction has still not been elucidated. It is believed that the principal stage is the decomposition of the complex of the substrate with LTA[149–152] involving a cyclic transfer of an electron pair, which results in the immediate formation of the two-electron oxidation product. The intermediate formation of a benzyl derivative of lead, i.e. plumbation of the side chain, has actually been suggested:



On irradiation (at 20–30 °C) and at temperatures above 80 °C, the reaction has a distinct radical character. Thermal[149,151,153] and photochemical[143,144,154] decomposition of lead(IV) carboxylate is accompanied by decarboxylation and the formation of aryl or alkyl radicals. The rate of decarboxylation increases in the presence of pyridine[144] and alkali metal acetates[101] and halides[144]. In conformity with mechanism (3), LTA oxidises toluene in acetic acid at 100 °C with formation of benzyl acetate, a mixture of xylenes, methylbenzyl acetates, and toluooylacetic acid[153]. The yield of benzyl acetate increases with increase of the ratio PhMe/AcOH and diminishes with increase of reaction temperature. Benzyl acetate is also formed in the photochemical reaction at room temperature[143,144]. Under these conditions, benzene gives rise to a mixture of toluene, benzyl acetate, and bibenzyl[145].

It is of interest that, when *p*-toluic acid is refluxed with LTA in trifluoroacetic acid in the presence of alkali metal chlorides or bromides, products of the oxidative halogenation of the aromatic ring are formed in high yields—3-halogeno-4-methylbenzoic acids[54]. Since the selectivity of this reaction is extremely high (>90%) for a purely radical process, the authors[54] do not rule out an appreciable contribution of the reaction via mechanism (8) with participation of mixed halide–arenecarboxylate complexes of lead [cf. the analogous reaction for cerium(IV)—see above].

In the presence of radical reaction initiators (monomethyl oxalate, di-isopropyl peroxydicarbonate), even substrates such as anisole can be oxidised via a radical mechanism[146]. The reactions with lead(IV) tetracarboxylates proceed under these conditions via the mechanism



It has been shown that, when the products (XXXI), (XXXII), and (XXXIV) are formed via mechanism (3), acyloxylation involves the intermediate formation of an anisole radical-cation [see mechanisms (1) and (8)]. The radical $PhOCH_2^{\bullet}$, formed from this radical-cation, reacts with the substrate to give compound (XXXIII).

Lead(III) derivatives formed via the mechanisms

$$RCO_2Pb(IV) \rightarrow R^{\bullet} + CO_2 + Pb(III)\ ;$$
$$R^{\bullet} + RCO_2Pb(IV) \rightarrow [R^+] + RCO_2Pb(III)$$

play an important role in the radical reactions. These derivatives act further either as one-electron oxidants or as sources of radicals[144,146].

As already mentioned above, one-electron oxidation processes, particularly acyloxylation in the ring and in the side chain and the formation of diarylmethanes in oxidative coupling reactions, compete with electrophilic and radical substitution processes. The role of such reactions increases with diminution of the ionisation potential of the substrate and with increasing electrophilicity of the oxidant. As for cobalt(III) (see above), LTA in an AcOH–$HClO_4$ mixture[45]

and lead(IV) trifluoroacetate in dichloroethane[49] oxidise mesitylene, pseudocumene, durene, and other methylarenes only to diarylmethanes. In contrast to toluene, 2-methylnaphthalene undergoes ring acetoxylation on treatment with LTA in acetic acid to a greater extent (~33%) than α-acetoxylation (~16%) or α-oxidation (~11%).[128] Finally at 105 °C LTA in acetic acid oxidises selectively the methyl group in 4-isopropyl-1-methylanisole to give the corresponding benzyl acetate in 55% yield[147].

8. Thallium(III)

The reactivity of thallium(III) salts depends greatly on the nature of the ligands. Thus the covalent thallium(III) sulphate and chloride are almost inert in reactions with aromatic hydrocarbons[155,156]. The slow reaction of alkylarenes with thallium(III) acetate in acetic acid is appreciably accelerated in the presence of H_2SO_4, HNO_3, BF, and particularly $HClO_4$.[156] The main product in the last case is the organothallium compound $ArTl(OAc)ClO_4.H_2O$. Biaryls, benzyl acetates (from methylarenes), bibenzyl (from PhMe), and diarylmethanes (in the case of *p*-xylene) are formed in smaller amounts[155,156].

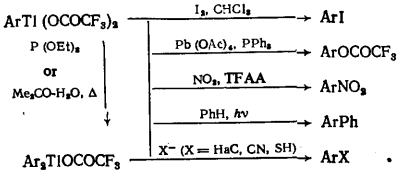
Under the same conditions, thallium(III) nitrate nitrates benzene (1.6%) and toluene (13%), but the reaction with *p*-xylene leads to a mixture of *p*-toluic acid (16.2%), toluic aldehyde (7.5%), and nitroxylene (6.1%).[156]

Thallium(III) carboxylates decarboxylated photochemically with formation of alkyl radicals. In the presence of benzene the photolysis of $Tl(OAc)_3$ gives a very low yield of a mixture of xylenes and phenylacetic acid[157].

The ionic thallium(III) trifluoroacetate (TTFA) shows the highest reactivity. The mode of its reaction with aromatic compounds is determined primarily by the oxidation potential of the substrate. Benzene, alkylbenzenes, and other compounds with fairly high ionisation potentials (>8 eV) react with TTFA to form products of S_EAr reactions—arylthallium bistrifluoroacetates[158–160].

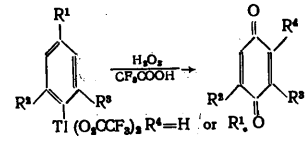
Dithallation on treatment with an excess of TTFA in TFAA has been observed only for anisole[161]. It is of interest that the monothallium derivative, formed in the presence of an equimolar ratio of the reactants (−25 °C, 15 min), is partly converted into 2,4-di(bistrifluoroacetoxythallium)anisole on standing for a week; the authors[161] explained this result by the stabilisation of the *o*-derivative as a result of the formation of a four-membered chelate ring. The thallation of 2,3,5,6-tetrafluoroanisole with TTFA does not occur in TFAA, but can be carried out in the presence of CF_3SO_3H.[162]

The kinetic and mechanistic aspects of thallation have been discussed in detail by Robey[155] and in reviews[158,160]. On the basis of arylthallium bistrifluoroacetates, McKillop and Taylor developed a whole series of valuable synthetic methods, particularly those represented schematically below:



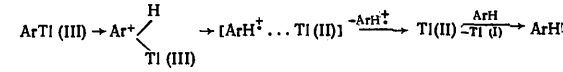
These reactions have been described in fair detail in reviews[159,160]. Methods have also been found for the synthesis of aryl fluorides [by treating compound (XXXV) with KF in the presence of BF_3][163] and areneboronic acids (by reaction with diboranes in tetrahydrofuran)[164].

Treatment of compound (XXXV) with a solution of 90% H_2O_2 in TFAA gives rise to *p*-quinones, the reaction being accompanied by the migration or elimination of substituents in the aromatic ring:



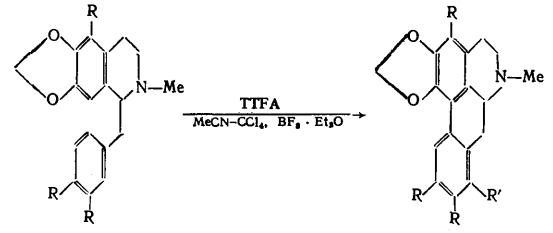
Elimination is observed for R^1 = Cl or OMe and also for R^1 = Me in the case of mesitylene. In other cases the group R^1 migrates to the 2-position (R^1 = H, Me, Et, or t-Bu)[165].

The final product of the reduction of thallium(III) is always a thallium(I) salt. In this case the transfer of two electrons [as for lead(IV)] can probably take place both synchronously and consecutively. According to Elson and Kochi[166], in the reaction of TTFA with alkylbenzenes thallium(III) acts as a one-electron oxidant and in the first stage gives rise via mechanism (1) to radical-cations of aromatic substrates, which were detected by EPR [the authors[166] also noted that thallium(III) makes it possible to generate a wide variety of radical-cations under static conditions, in contrast to the reaction of cobalt(III), which requires the use of a flow technique[47]]. Further reactions of the complex $ArH^{\ddagger}$ ... Tl(II) can be described by the following mechanism[167], depending on the substrate:



The reactions of TTFA via mechanisms (1) and (9) with substrates having low ionisation potentials (<8 eV) (polyalkoxybenzenes, naphthalenes, etc.) in TFAA, CCl_4, and acetonitrile give symmetrical biaryls in yields up to 99%.[167] The oxidation of durene in TFAA[167] and of *p*-xylene in the $Tl(OAc)_3$–AcOH–$HClO_4$ system leads to the formation of diarylmethanes[44,45].

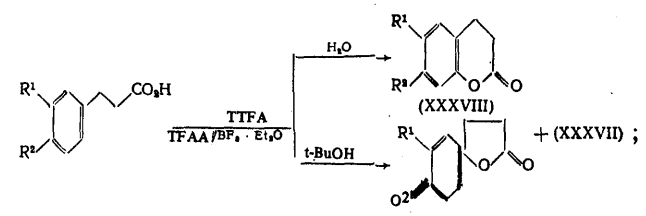
Oxidative coupling can also take place intramolecularly[168], which has been used, in particular, in the synthesis of alkaloids of the type of homoaporphine and aporphine (XXXVIa):



(XXXV) (a) R′ = H, (b) R′ = OAc

It is of interest that the replacement of TTFA by $Tl(OAc)_3$ leads to the ring acetoxylation product (XXXVIb) under the same conditions[168].

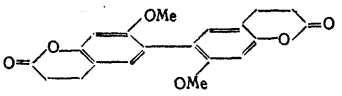
One should also note that the aromatic radical-cation can react intramolecularly with a carboxy-group to form dihydrocoumarins (XXXVIII) and spirolactones (XXXIX) [(XXXVII) : (XXXIX) = 3 : 1]:[169]



(XXXVI) (XXXVIII) (XXXIX)

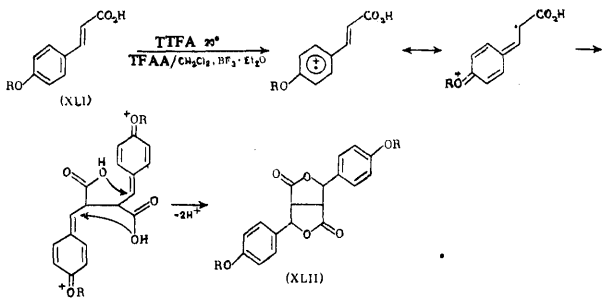
(a) $R^1 = R^2 = OMe$; (b) $R^1 = OMe$, $R^2 = H$; (c) $R^1 = H$, $R^2 = OMe$.

Not only the presence of the CO_2H group [the methyl ester of the acid (XXXVIIa) yields only the corresponding 2,2-biaryl] but also the position of the methoxy-group is important for the course of the reaction. Thus, under the reaction conditions, compound (XXXVIIb) only dimerises, while compound (XXXVIIc) gives rise to the product (XL) of simultaneous cyclisation and dimerisation[169]:



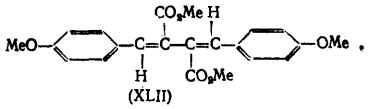
(XL)

The synthesis of the bislactone (XLII) is also extremely elegant[170]:



(XLI) (XLII)

The unsubstituted acid PhCH = CHCOOH does not react via this mechanism, while the methyl ester of the acid (XLI) yields the diene (XLII) as a result of the deprotonation of the radical dimerisation product:

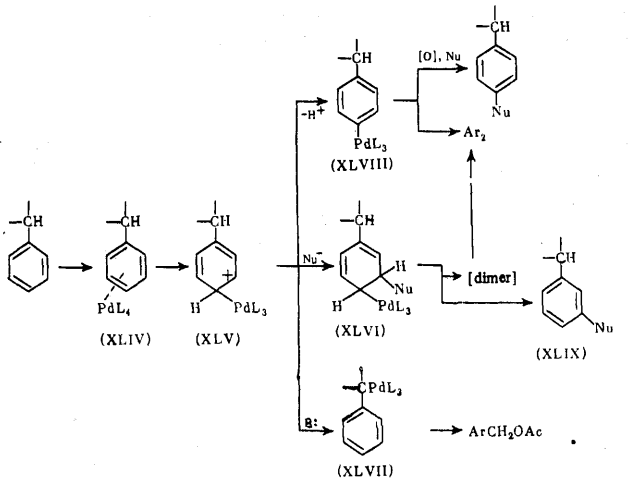


(XLII)

9. Palladium(II)

Palladium occupies a special place in the series of oxidants examined. Having the lowest oxidation potential, it exhibits the maximum selectivity in reactions with aromatic compounds and readily undergoes secondary oxidation on treatment with fairly mild oxidants, which makes it possible to use it in catalytic processes. On the other hand, the chemistry of palladium complexes is the most complicated and the mechanisms of its reactions are still controversial. The extensive applications of palladium(II) complexes in fine organic synthesis and technological processes have been described in a number of monographs[101,171,172] and reviews devoted to acetoxylation[128,173] and oxidative coupling[50,173,174] and for this reason the present review includes mainly general postulates concerning the mechanisms of the reactions of palladium(II) and new data not included in the reviews mentioned above.

The rate and mode of the reactions of alkylarenes with palladium(II) complexes depend very markedly on the composition of the palladium(II) coordination sphere. According to the existing ideas[171-175], the first stage in these reactions is the formation of the π-complex (XLIV) which, depending on the reaction conditions, is then converted into a σ-arylpalladium intermediate (XLV) and is attacked by a nucleophile with formation of the adduct (XLVI) or (in the presence of α-hydrogen and under the influence of a base) is converted into an α-substitution product—the benzylpalladium intermediate (XLVII):

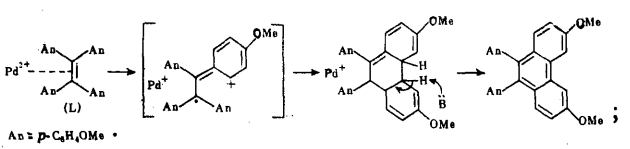


(XLIV) (XLV) (XLVI) (XLVII) (XLVIII) (XLIX)

On the basis of a comparison of the kinetics of the oxidative coupling and arylation reactions of olefins in the presence of palladium(II), it has also been suggested that palladium(II) can be inserted in the aromatic C—H bonds with formation of the species $ArPdH^{2+}$, whose stability has been explained[176] by the presence of a three-centre two-electron bond. According to the authors[176], a reaction of this type may constitute an intermediate stage in the slower reaction involving the formation of compound (XLVII), but there are as yet no data confirming this hypothesis.

The formation of π-complexes of benzene with $PdSO_4$ in 90% H_2SO_4 (23 °C) has been confirmed spectroscopically[177]. According to Rudakov et al.[177], the decomposition of these complexes leads to oxidative coupling products, benzene, and benzyl complexes of palladium(I), whose hydrolysis gives rise to zerovalent palladium, palladium(II), and benzene in proportions of 1:1:2.

The electron transfer in complexes of type (XLIV) proceeds, according to Eberson and Gonzalez[175], only in the presence of bases. Thus, on treatment with water, the complex (L) decomposes with liberation of the π-donor (tetra-anisylethylene), but on treatment with a stronger base (lutidine) it gives rise to an oxidation product:



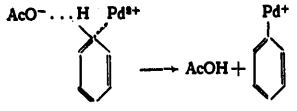
An = p-C_6H_4OMe .

The deprotonation of the complex (XLV) leads to the S_EAr reaction product—the arylpalladium compound (XLVII), which then decomposes with formation of a biaryl. The detailed mechanism of the last reaction is still not clear. It is

known that palladium(II) halides are inert in reactions with alkylarenes and that only $PdCl_2$ gives rise to oxidative coupling products in the presence of a fivefold excess of an alkali metal acetate in acetic acid[171-181]. It is believed[174,175,179-181] that the reaction proceeds in this case via the intermediate (XLVI) and involves its dimerisation with formation of bridge bonds involving chloride ions. The subsequent decomposition of the dimer gives rise to biaryl, zerovalent palladium, palladium(II), and acetic acid (Nu = OAc). At the same time the rate of oxidative coupling increases greatly in the presence of $HClO_4$, whereupon AcO^- is displaced from solution and the reaction proceeds via the usual S_EAr mechanism ($k_H/k_D = 5$ has been obtained for C_6H_6 and C_6D_6 [179,181] as in mercuration). It is believed[179] that in this instance the coupling reaction proceeds via a stage involving the formation of a mixed arylpalladium(II)–arene complex:

$$[Ar{-}Pd^+ \ldots ArH] \rightarrow Ar{-}Ar + H^+ + Pd\,(0)\ .$$

On the basis of the study of the kinetics of the oxidation of PhH to Ph_2 with palladium(II) perchlorate in the H_2O–AcOH–$HClO_4$ mixture[176], it is concluded that the rate-limiting stage of the reaction under these conditions is electrophilic attack on the aromatic ring by the $Pd(OAc)^+$ ions with simultaneous proton transfer to the coordinated or free acetate ion:



The σ-phenylpalladium cation disproportionates further to zerovalent palladium, palladium(II), and Ph_2. The rate of reaction decreases when acetic acid is replaced by TFAA and when Cl^- or Br^- is introduced. The activity of palladium(II) adsorbed on a carboxylic acid cation-exchange resin increases with increasing fraction of neutralised carboxy-groups[178].

The presence of an excess of acetate ions is not, however, essential for oxidative coupling. The complexes of $PdCl_2$ with ethylene, styrene, and cyclohexene give rise to Ph_2 in yields of 99, 63, and 3% respectively on oxidation of benzene, i.e. the yield varies in parallel with the decrease of the stability of the complexes (the yield in the absence of the olefin is 40%). The activity thus depends on the rate at which benzene exchanges with the olefin and $AgNO_3$ plays the role of a chloride ion acceptor and the co-oxidant (NO_2 is evolved in the reaction)[182,183].

Oxidative coupling under the influence of palladium(II) salts takes place readily with organic derivatives of boron, thallium, mercury etc., the arylpalladium intermediates being formed as a result of the substitution of the metal by palladium[171-174].

The scope of the method is extended by the fact that substituents in the aromatic ring have only a weak influence on the rate of the coupling reaction ($\rho = -0.4$).[184] A whole series of methods of synthesis of biaryls under the influence of palladium(II) complexes (including the sulphate and carboxylates[50,171-174,178] and the β-diketo-complexes[185,186]) in combination with thallium(III) and mercury(II) salts[187,189], metallic copper[188], and zirconium compounds[192] in stoichiometric[50,175,181] and catalytic[174,190] amounts in solvents (usually acetic acid) or in their absence[174,190] have been developed. The side reactions in the oxidative coupling (usually acetoxylation—see below) are effectively suppressed when the process is carried out under oxygen pressure (50–100 atm), which renders catalytic oxidation methods especially promising. In particular, the presence of heteropolyacids (HPA)—compounds soluble in water and organic solvents (HPA can contain phosphorus, silicon, arsenic, boron, etc.; the vanadium, molybdenum, and tungsten compounds are the most reactive) makes it possible to regenerate palladium at lower O_2 pressures (~25 atm) and in the absence of Cl^- ions and thus to avoid the chlorination of the substrate[191].

The second pathway in the decomposition of the intermediate (XLVI) involves its conversion into the product (XLIX) of nucleophilic substitution in the ring. The formation of acetoxy- and nitro-arenes under the influence of palladium(II) nitrate in acetic acid probably proceeds via this mechanism[192]. The addition of H_2O, $HClO_4$, and iron(III) salts shifts the reaction towards oxidative coupling.

Benzene, toluene, and chlorobenzene can be nitrated with preparative yields in the $Pd(NO_3)_2$–$NaNO_2$ and $Pd(OAc)_2$–$NaNO_2$ systems (100 °C, RCOOH; R = t-Bu, Me, or $ClCH_2$).[193] The reaction leads to a mixture of nitro- and acyloxy-arenes, the yield of nitration products being a maximum when palladium(II) and $ClCH_2COOH$ are used. On replacing $NaNO_2$ by N_2O_4, the nitration reaction in the presence of $Pd(OAc)_2$ takes place under catalytic conditions[193]. The analogous reaction in acetic acid (100 °C) yields in the case of benzene a mixture of nitrobenzene and phenyl acetate, whose proportions vary from 1:2 to 2:1 depending on the conditions[194].

The acetoxylation of alkylarenes under the influence of palladium(II) acetate requires, according to Eberson and Gonzalez[175], the involvement of the monomeric $Pd(OAc)_2$. The trinuclear cluster $Pd_3(OAc)_6$ is stable in the solid state and in acetic acid at temperatures below 35 °C (in benzene—below 80 °C) and decomposes on treatment with acetates [the monomeric $Pd(OAc)_2$ is formed on treatment with Et_4NOAc, while alkali metal salts give rise to the dinuclear complexes of $Pd(OAc)_2$ or MOAc promoting α-acetoxylation—see below][175].

In the absence of an excess of AcO^- the "nuclear" acetate can be obtained as the main product ($MeArOAc/HArCH_2OAc = 7/3$) when MeArH in boiling acetic acid is treated with $Pd(OAc)_2$ in the presence of O_2.[175] Although the reaction is catalytic, it is too slow for practical purposes[175]. In conformity with the structure of compound (XLVI), acetoxylation takes place preferentially in the *m*-position in the presence of *o*- and *p*-directing substituents in the substrate molecule (naphthalene gives rise to a mixture of different amounts of α- and β-acetates). The yield of aryl acetate greatly increases in the presence of co-oxidants. The best results were obtained for $Pd(OAc)_2$ using $K_2Cr_2O_7$, but LTA, $KMnO_4$, CrO_3, ClO_3^-, and O_2 are also fairly effective[195-198]. The isomeric composition of the ring acetoxylation products is determined under these conditions by the ratio of the rates of oxidation of the arylpalladium intermediates (XLVI) and (XLVII) and depends both on the reaction conditions (the yield of the *m*-isomer usually increases with increase of reaction temperature[195-198]) and on the nature of the co-oxidant).

In the presence of $Hg(OAc)_2$ the first stage involves the mercuration of the substrate. The subsequent transmetallation leads to compound (XLVII), whose oxidation in the presence of AcO^- gives rise to the acetoxylation product which retains the structure (XLVII). Thus mainly *p*-cresyl acetate is formed from toluene in the $Pd(OAc)_2$–$Hg(OAc)_2$–$K_2Cr_2O_7$ system[195]. The modification of this reaction using mercury derivatives of arenes and a number of nucleophiles makes it possible to obtain a wide variety of oxidative nucleophilic ring-substitution products (Nu = OAc, N_3, Cl, Br, NO_2, CN, or SCN).[193]

Potassium peroxydisulphate is particularly effective as a co-oxidant in the presence of palladium(II) complexes with

N-containing ligands (2,2-bipyridyl, pyridine, and isoquinoline), the ratio *o*/*p* amounting to 39/6 for pyridine and 5/44 for 2,2-bipyridyl [198] for the same yield of the *m*-isomer in both cases (54–51%).

An increase in the number of alkyl substituents in the substrate molecule shifts the reaction in the $K_2S_2O_8$–AcOH–$Pd(OAc)_2$–2,2′-py_2 system towards α-acetoxylation, whose contributions for toluene and *o*- and *p*-xylenes amount to 10, 39, and 86% respectively. Under these conditions, mesitylene and durene produce only the corresponding benzyl acetates under these conditions. The yield of the α-acetoxylated products also increases in the presence of an excess of acetate ions[196–198].

The practical value of the ring-acetoxylation process is very great, in particular as regards the development of methods for the direct oxidation of arenes to phenols. We may note that the oxidation of benzene to phenyl acetate via the reaction $PhH + AcOH + \frac{1}{2}O_2 \rightarrow PhOAc + H_2O$ requires the use of metallic palladium in combination with bismuth, selenium, cadmium, iridium, rhodium, ruthenium, and gold (in the latter case the conversion of PhH reaches 70–75%),[172] while according to the data of Venkateswar and Rao[199] the analogous process involving $PdCl_2$ on SiO_2 [in the presence of NaOAc and $Cd(OAc)_2$ at 170 °C] gives PhOAc in 8.43% yield and a selectivity of 100%.

The acetoxylation of a side chain constitutes yet another pathway in the reactions of alkylarenes with palladium(II) salts. In the absence of co-oxidants an increase of the AcO^- concentration and the $PdCl_2$–MOAc–AcOH–ArMe leads to the suppression of the oxidative coupling by α-acetoxylation. In the oxidation of toluene the ratio $MeC_6H_4C_6H_4Me$: $PhCH_2OAc + PhCH(OAc)_2$ changes from 38 to 0.0074 as the ratio NaOAc/$PdCl_2$ varies from 5 to 20.

According to Eberson and Gonzalez's data[175], α-acetoxylation is promoted by the formation of dinuclear complexes, which give rise to steric hindrance to attack by an external nucleophile in the stage of the intermediate (XLIV) or favour the reaction involving the formation of $ArCH_2OAc$ when the nucleophile is bound in the π-complex (XLIV) as the ligand. The yield of the substituted benzyl acetate depends both on the amount of MOAc and on the nature of the M^+. In most cases the maximum activity is shown by Pd/Rb system[175].

α-Acetoxylation is favoured by the addition of Ph_3P, in the presence of which two stable benzylpalladium complexes of the type of (XLVII) have been isolated[175]: $PdCl(Ph_3P)_2 \cdot CH_2Ph$ and $Pd_2Cl_2(Ph_3P)_2(CH_2Ph)_2$. On treatment with potassium acetate in acetic acid, both compounds give rise to benzyl acetate, while treatment with silver acetate under the same conditions results in the formation of benzyl acetate and benzylidene acetate.

In contrast to the weak influence of substituents on the rate of oxidative dimerisation[182,184], the "benzyl" oxidation depends markedly on this factor. Thus the reaction of PhMe with $Pd(OAc)_2$ in acetic acid (at 90 °C) leads to $PhCH_2OAc$ (80%), PhCHO (4%), and $PhCH(OAc)_2$ (6%), while p-$CH_3C_6H_4CH_3$ gives rise to 96% of the corresponding benzyl acetate and p-$NO_2C_6H_4CH_3$ gives 2% of this derivative[200].

Under these conditions, xylenes form a mixture of α-acetate and α,α- and α,α′-diacetates[180]. *o*- and *m*-Xylenes react more slowly than *p*-xylene but yield analogous products. The reactivity of methylarenes decreases in the sequence toluene > xylene > mesitylene > durene > hexamethylbenzene, i.e. contrary to the ability of the substrate to generate the radical-cation.

In the presence of $Sn(OAc)_2$ and solid carriers with a high surface area (wood charcoal, Al_2O_3) the acetoxylation of toluene under oxygen pressure becomes a catalytic reaction[171,172]. According to the data of Starchevskii et al.[201], the active centres under these conditions are cluster species containing palladium in the lowest oxidation states and not palladium(II) complexes.

The influence of oxygen on reactions in the $ArCH_3$–$PdCl_2$–MOAc–AcOH system has not so far found a satisfactory explanation. In the presence of O_2 and for low values of the ratio $AcO^-/PdCl_2 \cong 5$, the rate of oxidative coupling increases and acetoxylation slows down[172,175]. On the other hand, inhibition is not complete even at 50 atm O_2 [175] (the radical reactions of LTA, for example, are inhibited by even traces of molecular oxygen[175]), while the replacement of $PdCl_2$ by $Pd(OAc)_2$ results in the formation of aryl acetates in the presence of O_2 as the main reaction products[175]. Furthermore, the inhibiting effect of O_2 is absent for higher values of $AcO^-/PdCl_2$, amounting to 10–20, and under these conditions α-acetoxylation can be carried out catalytically (see above). Finally, on oxidation in the presence of O_2, aldehydes are formed only in the case of polymethylbenzenes[175]. The role of oxygen complexes of palladium(II) and zerovalent palladium[175] has so far been scarcely investigated in these reactions.

As for other oxidants, palladium(II) trifluoroacetate occupies a special place[202,203]. Trifluoroacetoxylation proceeds smoothly only in the case of naphthalene (120 °C) and yields exclusively 1-naphthyl trifluoroacetate[150] (the acetoxylation of naphthalene requires increased temperatures and gives rise to a mixture of two isomers—see above). In the case of benzene the analogous reaction proceeds in the presence of alkali metal trifluoroacetates and is suppressed by water[203]. In the absence of additives, fluoro-, chloro-, and nitrobenzenes give rise to biaryls, while benzene produces biphenyl and terphenyl (the relative yields depend on the reaction time)[203]. In the reaction with $Pd(OAc)_2$ in TFAA alkylarenes form mixtures of biaryls and diarylmethanes in the case of toluene, xylenes, hemimellitol, and pseudocumene, while in the case of durene and mesitylene biaryls are formed exclusively[204].

* * *

Thus analysis of the literature data shows that the oxidation of aromatic compounds by variable-valence metal complexes has been the subject of increasing attention by investigators during the last fifteen years. The range of reactions in which aromatic substrates can be involved is extremely wide and their products, which are in many instances obtained in preparative yields and are distinguished by a high selectivity, are just as varied. In addition to clearly synthetic problems, these processes make it possible to solve problems associated with the reactivity of highly active intermediates—aromatic radicals, radical cations, cations, as well as organometallic compounds and charge-transfer complexes.

There is no doubt that further development of this field of transition metal chemistry will prove to be extremely fruitful for the development of new synthetic methods and syntheses of compounds with valuable properties, for example, bifunctional monomers, derivatives of biphenyl and diphenylmethane, and phenols.

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Rearrangements in Vinyl Cations

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The literature data on the rearrangements of vinyl cationoid intermediates arising in the solvolysis of various vinyl derivatives and in the addition of cationoid reagents to the triple bond are examined and the differences between the rearrangements of vinyl cations and those of the "usual" saturated carbonium ions are demonstrated. The influence of the structure of vinyl cationoid intermediates on the rate and mode of rearrangements of various types (the migration of alkyl and aryl groups, shifts via the double bond and to a double bond, and higher-order shifts) are discussed. The bibliography includes 87 references.

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I. INTRODUCTION

Vinyl cations belong to the class of "hot" carbonium ions and it proved possible to detect them by NMR [1-4] as species stable in solution only in isolated instances. The chemistry of vinyl cations (VC) is therefore developing at the present time mainly on the basis of the study of the characteristics of reactions occurring under conditions most favourable for the formation of cationoid intermediates of the VC type. Either the solvolysis of vinyl derivatives containing readily removable groups such as triflate [trifluoromethanesulphonate(OTf)] or nonaflate [nonafluorobutanesulphonate (ONf)] or the addition of cationoid reagents to the triple bond are usually employed. In both cases it is better to use polar and non-nucleophilic media.

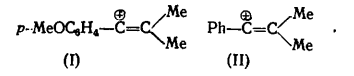
The question of the validity of the hypothesis of the intermediate formation of VC in these processes is by no means always clear, because it is sometimes difficult to exclude the possibility of alternative pathways leading to the formation of the observed products, for example, the elimination–addition or addition–elimination mechanisms in the solvolysis of vinyl derivatives or the synchronous Ad_E3 mechanism in the addition to the C≡C bond.

The choice between possible mechanisms is usually made on the basis of the study of the kinetics and stereochemistry in combination with data on the composition of the reaction products formed under various conditions. However, one of the principal criteria indicating the intermediate formation of VC is as a rule the observation of sextet rearrangements. Although, strictly speaking, this criterion does not constitute total proof, it has been used traditionally also in the more general case involving the study of the mechanisms of any reactions with possible involvement of carbonium ions as intermediates.

The characteristics of sextet rearrangements of the "usual" carbonium ions have been studied very widely and have been considered in detail in a series of monographs and reviews[5-8]. The data on the rearrangements of VC are much more scanty and limited, but in recent years numerous instances of reactions of this kind have been described and in the present review an attempt is made to survey these data†.

† Different aspects of the chemistry of VC have been examined in a series of reviews[16-23] published recently, which reflects the enhanced interest in these intermediates.

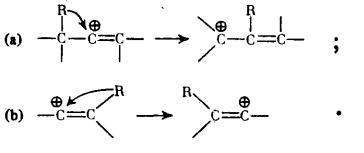
In discussing the characteristics of the rearrangements of C≡C, it is necessary to have a clear idea about their structure. At the present time this problem has still not been adequately investigated experimentally, although the available calculations in the literature[9-12] have shown that a linear structure with an *sp*-hybridised carbon atom having a positive charge is preferred for VC. This structure of VC has been confirmed[1,4] by ^{13}C and ^{1}H NMR for VC (I) and (II) in which the alkyl groups proved to be equivalent:



(I) (II)

The results of solvolytic reactions also indicate a linear structure of VC. Thus the rate of solvolysis of cycloalkenyl triflates in 50% aqueous ethanol solution at 75 °C increases with increase of ring size, while the the cyclo-octene derivative it becomes comparable to the rate solvolysis of (*E*)-1-methyl-1-propenyl triflate[13-15]. The relatively low rate of solvolysis of cyclohexenyl triflate can be explained by the impossibility of attaining a linear geometry in the vinyl-cation-like transition state in rings of this size.

The examples of rearrangements in vinyl-cationoid intermediates (VCI) available at the present time are mainly 1,2-shifts and can be divided into two large groups: (a) rearrangements with migration to the double bond leading to allyl cations and (b) rearrangements via the double bond, as a result of which one VC isomerises to another:



The less numerous rearrangements occurring as a result of higher-order shifts do not fit within the framework of this classification, because they involve simultaneously saturated and unsaturated fragments of the molecule and their usual result is the formation of a carbonium ion centre at a saturated carbon atom.

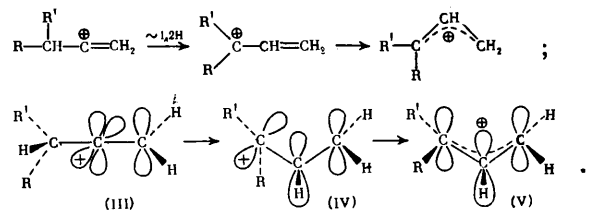
For each of the above type of rearrangements, there is a possibility of a more detailed classification based on the atoms or groups which migrate under these conditions.

II. REARRANGEMENTS WITH MIGRATION TO THE DOUBLE BOND

1. The 1,2-Hydride Shift

The hydride shifts in the chemistry of the "usual" carbonium ions are very common and usually take place extremely readily (the activation barrier to such rearrangements is frequently less than 12–16 kJ mol^{-1}). For example, the 1,2-hydride shift in the 2-butyl cation is so fast compared with the NMR time scale that even at −120 °C only a single average signal due to the CH_3 group is observed in its ^{1}H NMR spectrum[24].

The 1,2-hydride shifts in VC take place with much more difficulty and have been described for a fairly limited number of examples. This fact may appear fairly strange since this type of 1,2-shift should result in the conversion of an unstable VC to the stabilised system of the allyl cation and hence the thermodynamic driving force of such rearrangements should be fairly considerable. However, the difficulty of the 1,2-shifts in VC can be explained by considering the stereochemistry of the orbital interactions in this process. Indeed the conversion of the linear VC (III) into the planar resonance-stabilised allyl cation (V) should proceed via a non-planar transition state (or intermediate) (IV), in which resonance stabilisation is impossible and which is additionally destabilised by the presence of an orthogonal π-system:

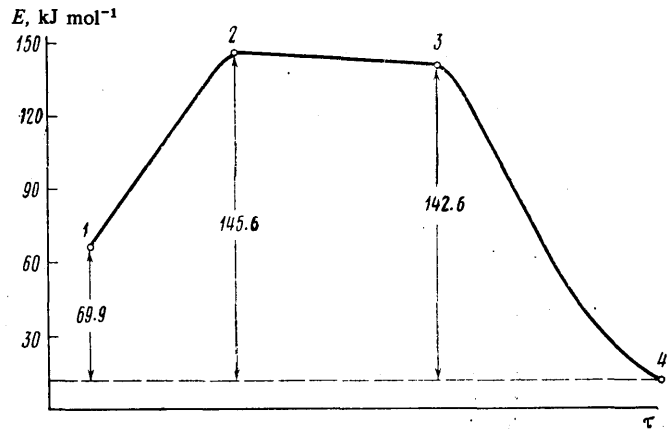


This is apparently why the activation barrier to the above process is in fact significantly higher than for the 1,2-shift in the "usual" carbonium ions.

The energetic pathway of the 1,2-hydride shift in VC, obtained[12] on the basis of the available calculations of the energies of the isomeric $C_3H_5^{\oplus}$ ions, is illustrated in the Figure.

The 1,2-hydride shifts in VC have been studied in greatest detail in connection with the protonation of alkynes in "magic" acid (FSO_3H–SbF_5). It has been found that in none of the instances investigated is it possible to observe directly (by ^{1}H NMR) the formation of VC even at low temperatures (−78 °C), although these conditions have almost always proved to be suitable for the observation of carbonium ions of other types. It has been shown that the result of the protonation of the triple bond, observed with the aid of ^{1}H NMR, is the formation of the allyl cation (produced by the unimolecular 1,2-hydride shift in the VCI) or an oligomeric product (a bimolecular process). The latter pathway is usually preferred when the reaction is carried out at low temperatures (78 °C). An increase of temperature as a rule leads to a significant increase of the yield of rearrangement products, which reflects the usual kinetics of unimolecular and bimolecular reactions.

The 1,2-hydride shift takes place most readily in VC formed from alkynes, in which there are two alkyl substituents at the α-carbon atom. The rearrangements in such alkynes take place at −20 °C. The activation barrier for such systems is lower than the value indicated in Fig.1 owing to the stabilising effect of the alkyl groups. In alkynes with only one alkyl substituent at the α-carbon atom the 1,2-hydride shifts take place at higher temperatures (7–20 °C). The protonation of alkynes without branches at the α-carbon atom is more complex and in this instance it is not possible to detect the formation of allyl cations introduced by the 1,2-hydride shift in the VC formed initially.

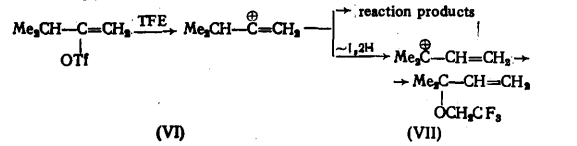


The energetic pathway of the 1,2-hydride shift in the vinyl cation:

1) $Me-\overset{\oplus}{C}=CH_2$; 2) $H_2C\overset{H}{\overset{+}{\cdots}}C=CH_2$; 3) $H_2\overset{\oplus}{C}-CH=CH_2$;

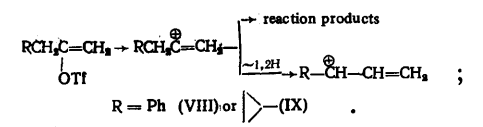
4) $H_2C\overset{CH}{\overset{+}{\cdots}}CH_2$.

The only other example in which a 1,2-hydride shift to the double bond is observed is the solvolysis of isopropylvinyl trifluoromethanesulphonate (VI) in trifluoroethanol (TFE). The ether (VII), which is believed[26] to be formed as a result of the 1,2-hydride shift in the VCI formation stage, was isolated together with the normal solvolysis products under these conditions:



However, the authors do not consider the possibility of its formation via the elimination–addition mechanism.

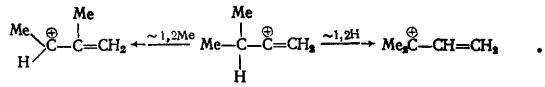
This result appears to be unexpected also because, for example, in the solvolysis of 1-benzylvinyl triflate (VIII) [27] and 1-cyclopropylmethylvinyl triflate (IX),[28] compounds which might be formed via a 1,2-hydride shift in the VCI are not detected among the products, although the presence of a stabilising substituent at the allyl carbon atom in the given systems should facilitate such a transition:



2. The 1,2-Shifts of Methyl Groups

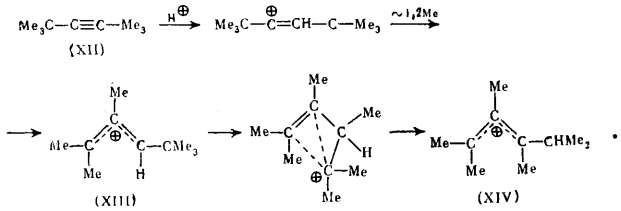
The characteristics of the 1,2-hydride shifts in VCI mentioned above, leading to an increase of the activation barrier compared with the rearrangements in the "usual" carbonium

ions, apply equally to the 1,2-shifts of methyl groups. In this instance too the number of examples is negligibly small compared with the number of studies on the 1,2-migrations in the "usual" carboniun ions. As will be seen from further exposition, the 1,2-shift of the methyl group is observed in compounds with a t-butyl substituent at the carbon atom with a positive charge. This is not surprising, since, in the presence of a hydrogen atom attached to an α-carbon atom, the hydride ion migrates, as has been observed in the protonation of alkynes[25], as a result of which the cation (X) formed is more stable than the alternative cation (XI):



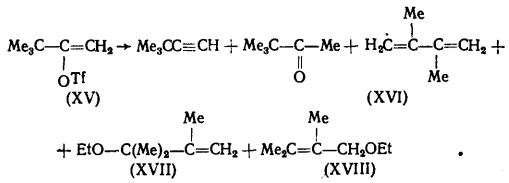
(XI) (X)

The protonation of t-butylacetylene and 2-t-butyl-1-methylacetylene at −20 °C in FSO_3H-SbF_5 leads to the formation of the corresponding allyl cations[25], which indicates the occurrence of 1,2-methyl shifts in the VCI formed initially. At a lower temperature (−78 °C) complex mixtures of oligomerisation products are formed in these reactions. However, the rearrangement involving the sterically hindered di-t-butylacetylene (XII) is observed also at −78 °C. In this instance the rearrangement is more far reaching and, instead of the signals of the allyl cation (XIII), the ^1H NMR spectrum shows signals due to the carbenium ion (XIV), which is apparently formed as a result of the rearrangement of the homoallyl cation:



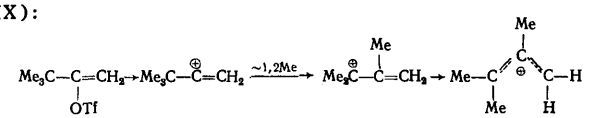
(XII) (XIII) (XIV)

The solvolysis of t-butylvinyl triflate (XV) in aqueous ethanol solution yields t-butylacetylene as the main product, but this is accompanied by the formation of 10–15% of 2,3-dimethylbutadiene (XVI) and of the rearranged alcohols and ethers (XVII) and (XVIII):[29]



(XV) (XVI) (XVII) (XVIII)

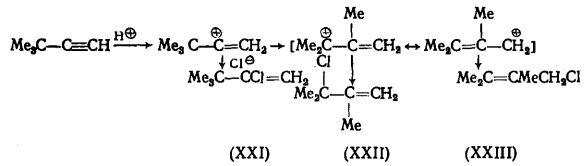
The products (XVI)–(XVIII) were obtained as a result of the 1,2-shift of the methyl group in the VC (XIX) formed initially and further transformations of the isomeric cation (XX):



(XV) (XIX) (XX)

Analogous products are formed also in the acetolysis of compound (XV). The study of this process in CH_3COOD showed that deuterium is not incorporated in the reaction products and the alternative mechanisms of the formation of these products via addition–elimination or elimination–addition processes do not therefore occur and a rearrangement in the VCI takes place[30].

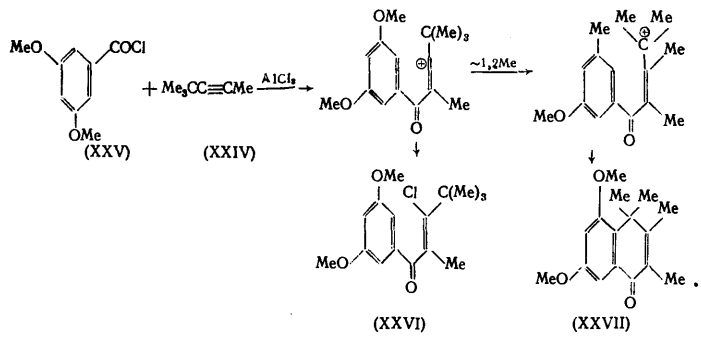
The addition of hydrogen halides to acetylenes is not usually accompanied by rearrangements[31], but in the interaction of t-butylacetylene with HCl without a solvent (the alkyne and dry HCl are mixed in a closed vessel at approximately −180 °C and the temperature is then raised to room temperature) the rearrangement products (XXII) and (XXIII) were isolated in 10–15% yield together with the normal reaction product (XXI):[32]



(XXI) (XXII) (XXIII)

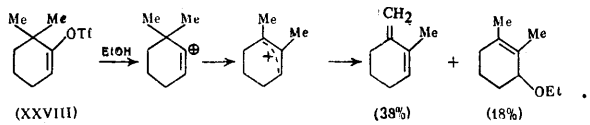
With increase of the amount of HCl to give a tenfold excess, the yield of rearranged products increases to 64%.

In the acylation of 4,4-dimethylpent-2-yne (XXIV) with 3,5-dimethoxybenzoyl chloride (XXV) in the presence of $AlCl_3$, 5–10% of the product of the 1,2-migration of the CH_3 group [compound (XXVII)] is formed together with β-chlorovinyl ketone (XXVI):[33]



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

The 1,2-migration of the methyl group has also been observed in the solvolysis of the cyclohexenyl triflates (XXVIII) with two methyl groups at the α-carbon atom[34]:

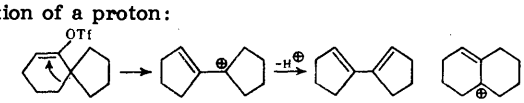


(XXVIII) (38%) (18%)

3. Rearrangements Involving a Change in the Cyclic System of Alicyclic Molecules

Most of the rearrangements involving an alteration of the skeleton of alicyclic compounds should be included in the class of rearrangements via the double bond of VC and these will be considered below.

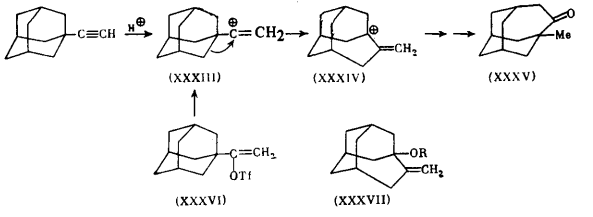
However, there are several examples which can be regarded as rearrangements with migration to the double bond. Thus the main product of the solvolysis of spiro-vinyl triflate (XXIX) in 60% aqueous ethanol or 50% aqueous TFE (in the presence of pyridine buffer) at 130 °C is the diene (XXXI). The authors[35] explain its formation by concerted ionisation and migration with the probable anchimeric participation of a bond of the cyclohexane ring in a convenient position, which leads to the formation of the carbenium ion (XXX) and the latter is converted into compound (XXXI) as a result of the elimination of a proton:



(XXIX) (XXX) (XXXI) (XXXII)

Important evidence in support of this concerted mechanism is the absence of compounds among the reaction products whose formation would have corresponded to the intermediate generation of the carbonium ion (XXXII). Its formation might have been expected by analogy with the above example of the migration of one or two geminal methyl groups in the solvolysis of compound (XXVIII). However, the virtually quantitative (>90%) yield of the diene (XXXI) shows that none of the spiroalkyl bonds of the cyclopentane ring in compound (XXIX) is involved in the migration.

Another example is the conversion of the adamantane system into the homoadamantane system. The hydration of adamantylacetylene catalyed by mercury salts takes place normally and leads to adamantyl methyl ketone[36]. However, in the protonation of adamantylacetylene with 90% H_2SO_4 in hexane at −5 °C 3-methyl-4-homoadamantanone (XXXV) is formed together with the normal product—adamantyl methyl ketone[37]:

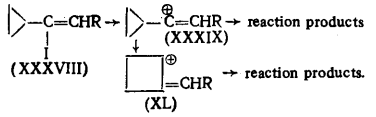


(XXXIII) (XXXIV) (XXXV)

(XXXVI) (XXXVII)

Its formation can be explained by the rearrangement of the adamantylvinyl cation (XXXIII) to the homoadamantyl cation (XXXIV). The solvolysis of the vinyl triflate (XXXVI) confirms the proposed mechanism of the rearrangement. Depending on the conditions of the solvolysis[30], the main products are either elimination products (in 60% ethanol and acetic acid with a buffer) or rearranged products (in TFE); thus the use of a less basic solvent promotes the rearrangement, which confirms that the latter takes place via the VCI (XXXIII). It was also shown that the further transformation of the cation (XXXIV) into the final reaction products proceeds under the influence of an acid, since in the solvolysis in TFE with a buffer the main reaction products were compounds of the type of (XXXVII, R = CH_2CF_3 or H). If the CF_3SO_3H evolved in the solvolysis is not neutralised, the above compounds rearrange to compound (XXXV). It must be emphasised that the driving force of the rearrangement of the VC (XXXIII) should apparently be considerable, since the increasing strain of the system on passing from adamantane to homoadamantane does not prevent the rearrangement.

The rearrangement with participation of the bonds of a cyclic substituent is observed also in the solvolysis (noncatalysed or catalysed with silver salts) of 1-cyclopropyl-1-iodovinyl compounds of the type of (XXXVIII):[38–40]:



(XXXVIII) (XXXIX) (XL)

Despite the fact that the cyclopropane ring has a stabilising influence in the given systems on the VC (XXXIX) formed initially, the latter partly rearranges to the allylic cyclobutyl cation (XL) and up to 14% of cyclobutane derivatives were detected among the reaction products. Study of the temperature variation[39] showed that the yield of the rearranged products increases with temperature.

III. REARRANGEMENTS VIA THE DOUBLE BOND

As stated above, in the 1,2-shifts via the double bond one VCI rearranges to another. Therefore the driving force of such rearrangements is the formation of a more stable VCI. Naturally the mode and extent of such rearrangements depend significantly, apart from other factors (the nature of the solvent, the nucleophiles present in the medium, etc.), on the stabilising influence of the substituents in both the initial and the rearranged VCI.

1. The 1,2-Hydride Shift

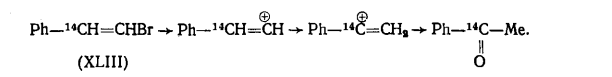
The 1,2-hydride shift of the type under consideration should take place most readily in those cases where the initial intermediate is the primary VC (XLI), since the conversion of the latter into compound (XLII) should be a thermodynamically favoured process [according to calculations for the gas phase, compound (XLII) is more stable to the extent of 67 kJ mol^{-1} than compound (XLI)]:[12]



(XLI) (XLII)

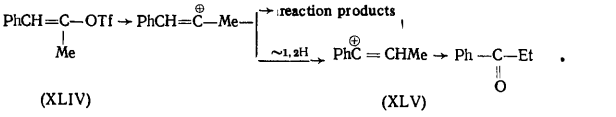
However, because of the low stability of the initial VC, the formation of this type of intermediate is unlikely and apparently occurs only in exceptional cases (see, for example, Hanack et al.[41]). Accordingly, mechanisms which do not require the intermediate formation of a primary VC are as a rule more justified in the interpretation of the results of the reactions.

For example, in the reactions of *cis*- and *trans*-β-bromostyrenes (XLIII) with $MeCO_2Ag$ in MeCOOH the formation of acetophenone as the main product (together with phenylacetylene) was observed[42]. It was also found that in the course of the reaction there is no 1,2-shift to the phenyl group and it was suggested that the hydride ion migrates in the VC:



(XLIII)

However, it was later established[43] that the successive elimination–addition mechanism is more probable for the solvolysis of both β-bromostyrenes and other similar substrates[44]. There is good reason to consider mechanisms involving VC in those cases where a secondary VC is formed initially. For example, in the solvolysis of (*E*)- and (*Z*)-1-methyl-2-phenylvinyl triflates (XLIV) the main products are an alkyne and an allene. However, they are accompanied by the formation of between 3 and 17% (depending on the conditions) of ethyl phenyl ketone (XLV), produced as a result of the 1,2-hydride shift via the double bond in the VCI:[43]

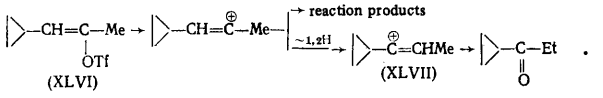


(XLIV) (XLV)

Although in the given instance synchronous elimination takes place to a considerable extent (this is manifested, in particular, by the higher rate of solvolysis of the *Z*-isomer compared with the *E*-isomer), ethyl methyl ketone (XLV) is not formed as a result of the hydration of methylphenylacetylene, since the latter is not hydrated under the reaction conditions and is isolated unchanged.

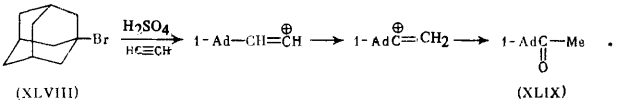
An analogous 1,2-hydride shift has been observed also in the solvolysis of (*E*)- and (*Z*)-2-cyclopropyl-1-methylvinyl triflates (XLVI).[26,45] The yield of cyclopropyl ethyl ketone

(XLVII), formed as a result of the rearrangement of the VCI, is 11–17%. In contrast to the previous case, in this instance the solvolysis via the formation of the VCI was not rigorously demonstrated, but the composition of the product and the ratio of the rates of solvolysis of the *E*- and *Z*-isomers suggest that the solvolysis does in fact proceed mainly via this mechanism:



It is of interest that, under comparable solvolysis conditions (3 : 2 or 4 : 1 TFE–H_2O mixture at 80 °C), the yield of ethyl phenyl ketone (4.7–5.9%) is smaller by a factor greater than two than the yield of cyclopropyl ethyl ketone (11.1 to 16.9%), which is associated, according to the authors[26,43], with the greater ability of the cyclopropane ring to stabilise the α-cationic centre.

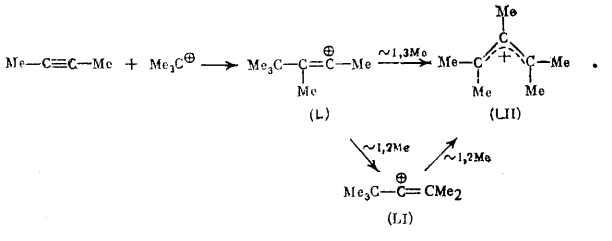
A 1,2-hydride shift via the double bond has also been suggested to account for the results of the reaction of 1-adamantyl bromide (XLVIII) with acetylene in H_2SO_4,[46,47] leading to the formation of 1-adamantyl methyl ketone (XLIX) as the main product (40%):



However, a vulnerable feature of this mechanism is undoubtedly the formation of the primary VC and the reaction probably proceeds in reality via a different pathway.

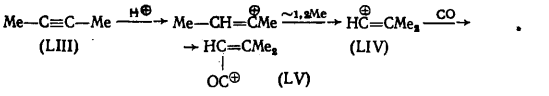
2. The 1,2-Shifts of the Methyl Groups

The ^1H NMR spectra of the products of the addition of the t-butyl cation (obtained via the reaction of t-C_4H_9Cl with $SbCl_5$ in SO_2) to but-2-yne showed[48] that, even at low temperatures (-75 °C), the pentamethylallyl cation (LII) is formed exclusively. It can be formed either as a result of a single 1,3-shift of the methyl group or as a result of two consecutive 1,2-shifts:



This problem was solved in the alkylation of but-2-yne by $(CD_3)_3CCl$; on the basis of the distribution of the D label, it was shown that the allyl cation (LII) is formed as a consequence of two consecutive 1,2-shifts of the CH_3 groups[48]. Thus this reaction is a unique example in which both types of rearrangements in VC are observed in succession: initially via the double bond [(L) → (LI)] and then via migration to the double bond [(LI) → (LII)]. This example also shows apparently that two consecutive 1,2-methyl shifts instead of a single 1,3-migration are preferable for VC, as for the "usual" carbonium ions.

A fairly unusual rearrangement has been observed[49] when a mixture of but-2-yne and CO was passed into the "superacid" medium ($FHSO_3$–SbF_5):

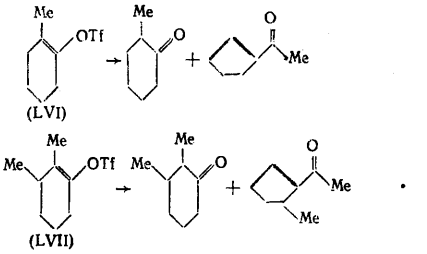


The acylium ion (LV), believed[49] to be capable of formation as a result of a 1,2-shift of the CH_3 group via the double bond, was detected (by ^1H NMR) among the reaction products. The reaction is unusual, because the VC (LIII) formed initially rearranges to a less stable VC (LIV), while in all the rearrangements described above the driving force is the formation of a thermodynamically more stable VC. It is appropriate to mention here that the carbonylation of the "usual" carbonium ions always leads to the formation of thermodynamically more stable isomers[50]. In the explanation of the course of the above reaction, the authors[49] attribute to SbF_5 a specific role in the formation of complexes with alkynes, which, however, appears to be unlikely.

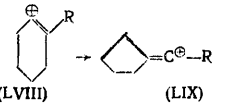
3. Rearrangements Associated with a Change in the Cyclic System of Alicyclic Molecules

The rearrangements of cyclic VC are characterised by a series of features due primarily to the fact that the mode and extent of the rearrangements are determined not only by the greater thermodynamic stability of the rearranged ion but also by the structure (ring size) of the entire alicyclic molecule.

The solvolysis of methyl-substituted cyclohexenyl triflates (LVI) and (LVII) yields a mixture of approximately equal amounts of the rearranged and non-rearranged products[13]:

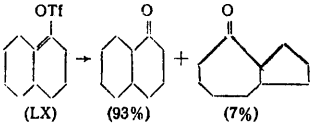


At first sight these results appear to be fairly strange, since a linear geometry is preferable for VC and the complete conversion of the VC (LVIII) into the VC (LIX) might have been expected:

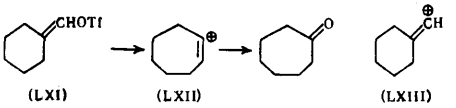


However, this transition is apparently prevented by the increasing strain in the methylenecyclopentane system compared with the cyclohexenyl system. It is also possible that cyclohexanone derivatives are not formed via VC but as a result of the dissociation of the S–O bond[51].

A much smaller degree of rearrangement is observed[13] in the solvolysis of the bicyclic vinyl triflate (LX):



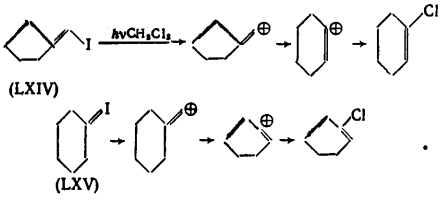
The rearrangements described above occur only in systems having a substituent at the β-carbon atom of the vinyl group. For the cations (LVIII, R=H), the rearrangement is hardly observed, because it would lead to the formation of very unstable primary VC of the type of (LIX, R=H), which, as stated above, is unlikely under the solvolysis conditions. The data on the solvolysis of the vinyl triflate (LXI), which results in the formation of 95% of cyclohexanone and 2.5% of formylcyclohexane, are consistent with these ideas:



(LXI) (LXII) (LXIII)

Cycloheptanone is probably formed via a mechanism involving concerted ionisation and the migration of an alkyl group, leading to the intermediate cycloheptenyl VC (LXII).[35] These results show that, despite the preferred linear configuration of VC, the bent secondary VC (LXII) is more stable than the linear primary VC (LXIII); hence it is clear how significantly the size of the VCI ring influences the mode and degree of the rearrangement.

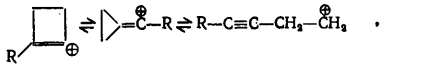
Rearrangements of a similar kind have been observed in studies of the photochemical transformations of vinyl halides which are believed to proceed via a stage involving the heterolysis of a carbon–halogen bond with formation of VC. Thus the photolysis of the vinyl iodides (LXIV) and (LXV) in methylene chloride results in the formation of considerable amounts of 1-chlorocyclohexene and 1-chlorocycloheptene respectively; this is believed[52] to occur as a result of a rearrangement via the double bond of the initial primary VC to the secondary VC, which subsequently abstract a chloride ion from the solvent molecule:



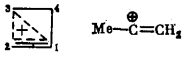
(LXIV)

(LXV)

Interesting examples of reversible transformations of the VCI, occurring as 1,2-shifts via the double bond, have been described by Hanack and coworkers[41,51,53], who investigated the solvolysis of cyclobutenyl nonaflates, bromomethylenecyclopropanes, and but-3-yn-1-ol derivatives. It was found that the composition of the products obtained is very insensitive to the nature of the substrate, which is consistent with the following mechanism of the transformation of carbonium ion intermediates:



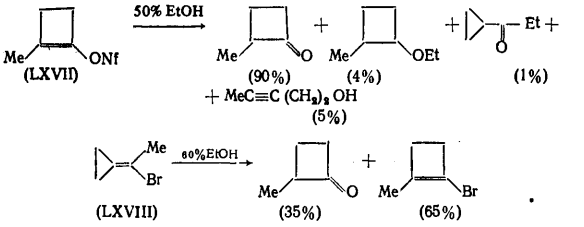
Bearing in mind that a linear geometry is preferable for the VC, the assumption that these transformations involve the cyclobutenyl cation, for which this type of geometry is impossible, appears fairly strange. However, it has been suggested[51] that the positive charge in the cyclobutenyl cation is delocalised over $C_{(2)}$ and $C_{(3)}$ as a result of the overlap of the vacant *p* orbital of the VC and the σ orbital of the $C_{(2)}$–$C_{(3)}$ bond:



(LXVI) (XLII)

The possibility of the formation of this non-classical structure (LXVI) has been confirmed by calculations[51] showing that its stability is comparable to that of the linear VC (LXII). The mode and degree of the rearrangements in the systems under consideration depend on the ability of the substituent R to stabilise the positive charge. Thus the only product of the solvolysis of cyclopropylidenemethyl bromide in the 1 : 1 water–ethanol mixture was cyclobutanone[53]. The same ketone proved to be the main product of the solvolysis of cyclobutenyl nonaflate[51]. On the basis of these data as well as calculations, the authors concluded that the cyclobutenyl cation is more stable than the cyclopropylidenemethyl cation.

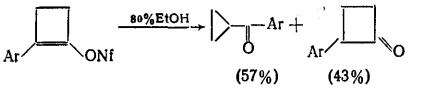
It is noteworthy that in these examples and those described above the carbonium ion mechanism has been fairly reliably demonstrated for solvolytic reactions of this kind. The absence of an addition–elimination process has been demonstrated by the independence of the solvolysis rate constant on the pH of the medium; furthermore, for certain reactions in labelled solvents, no incorporation of the isotope label was observed. In some cases[51,54] the ionic mechanism of the reactions was demonstrated by adding to the reaction mixture salts with an anion different from that of the leaving group. Under these conditions, both the initial and rearranged compounds containing the anion of the added salt were isolated; this demonstrates that the rearrangements proceed via the intermediate formation of ion pairs. The introduction of the methyl group in the 2-position of the cyclobutenyl ring exerts an additional stabilising effect on the cyclobutenyl cation formed, as shown by the considerable increase of the rate of solvolysis. The formation of cyclobutane derivatives as the main products in the solvolysis of 2-methylcyclobutenyl nonaflate (LXVII) and bromoethylidenecyclopropane (LXVIII) is believed[41,51] to show that the 2-methylcyclobutenyl cation is much more stable than the corresponding cyclopropylidene VC:



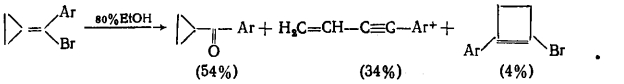
(LXVII) (90%) (4%) (1%) (5%)

(LXVIII) (35%) (65%)

The introduction of an aromatic substituent (a phenyl or anisyl group) in compounds (LXVII) and (LXVIII) instead of the CH_3 group alters significantly the composition of the products formed (cyclopropene derivatives constitute more than 50% of the mixture[51,55]):

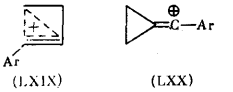


(57%) (43%)



(54%) (34%) (4%)

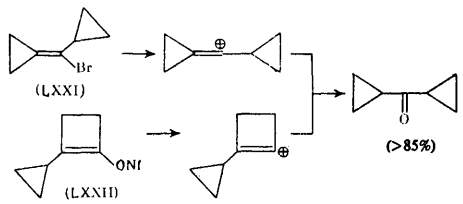
Thus the stabilising influence of the aromatic substituent on the cyclobutenyl cation (LXIX) is very insignificant:



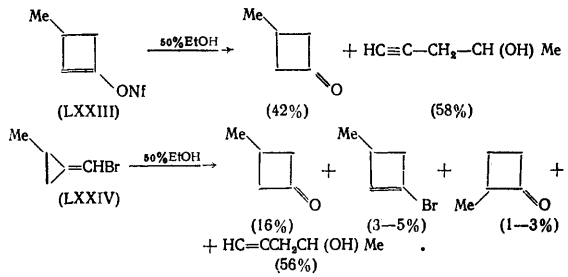
(LXIX) (LXX)

This is also indicated by the rate constants for the solvolysis of 2-arylcyclobutenyl nonaflates, which increase little compared with the rate constant for the unsubstituted derivative.

On the other hand, the VC (LXX) is stabilised significantly by an aromatic substituent. The stabilisation of this species by the cyclopropane ring is even greater, which is reflected in the composition of the solvolysis products of the cyclopropylcyclopropylidene bromide (LXXI) [41] or 2-cyclopropylcyclobutenyl nonaflate (LXXII): [51]



The main product of the solvolysis of these compounds in ethanol is dicyclopropylketone. The solvolysis of 3-methylcyclobutenyl nonaflate (LXXIII) leads to a mixture of 3-methylcyclobutanone and pent-1-yn-4-ol.[51] Derivatives of cyclobutane and the same alcohol have been isolated in the solvolysis of the *E*- and *Z*-isomers of 2-methylcyclopropylidenemethyl bromides (LXXIV),[56] both isomers giving rise to the same mixtures of products:



Thus in the given instances the 3-methylcyclobutenyl cation is more stable than the 2-methylcyclopropylidene cation.

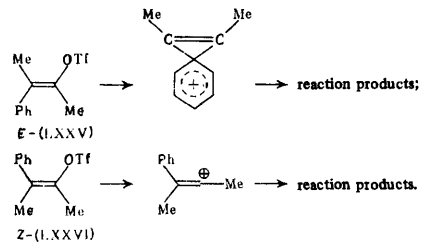
4. The 1,2-Shifts of Aryl Groups

The migration of aryl groups has been studied in greatest detail among the rearrangements of the VCI. This is quite natural because aryl-substituted VC in fact belongs to the most stable intermediates and the characteristics of the reactivity of these carbonium ions can be most conveniently studied on these models.

The usual method of synthesising VC of this type is solvolysis of various arylvinyl compounds; the study of the kinetics of this reaction and of data for the compositions of the products made it possible to elucidate a number of features relating to the migration of aryl groups via the double bond.

One of the principal problems in this connection is whether or not the migrating group is involved in the transition state of the heterolysis or whether the initial ionisation leads to a non-rearranged VC. Evidently in the general case the answer to this question depends to the greatest extent on the structure of the initial substances and particularly on their configuration. This has been studied in very great detail [57,58] in relation to the solvolysis of the *E*- and *Z*-isomers of 3-phenyl-2-but-2-enyl triflates (LXXV) and (LXXVI). The solvolysis of the *Z*-isomer in 60% aqueous ethanol gives rise to 33.5% of 3-phenyl-2-butanone and 66.5% of allene, while the *E*-isomer produces 82% of the ketone and only 18% of the allene; the rate of solvolysis of the *E*-isomer is twenty times higher than that of the *Z*-isomer.

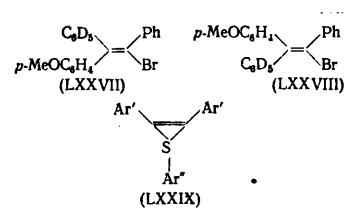
The solvolysis of these compounds in absolute TFE established the dependence of the mode of reaction on the stereochemistry of the initial compounds. To account for the different rates of reaction, the differences between the products, and their stereochemistries (the solvolysis in TFE yields the *E*-isomers in both cases), it has been suggested [57] that the *E*-isomer reacts preferentially if not exclusively with participation of the β-phenyl group and the formation of a bridged ethylidenephenonium ion as an intermediate. The *Z*-isomer yields initially a linear VC, which gives rise to a considerable amount of allene after the elimination of the proton. The formation of the *trans*-adduct in the solvolysis of the *E*-isomer in TFE confirms the formation of a bridged intermediate during the solvolysis, while it is believed [57] that in the case of the *Z*-isomer the VC forms an ion pair with the leaving group, which leads to a *trans*-adduct in the reaction with the solvent:



This mechanism was also confirmed in a study of the reactions with isotopically-labelled compounds (α- and β-CD_3 groups). The *E*-isomer then gives rise to compounds with a virtually complete redistribution of the D label, which was to be expected for the formation of an intermediate bridged carbenium ion, while in the reaction with the *Z*-isomer the degree of redistribution of the label is much smaller.

Further confirmation of the proposed mechanism was obtained in the study of the β-isotope effect (α-CD_3 group). It was found that the β-effect in the *Z*-isomer is very large (k_H/k_D = 1.47), while that for the *E*-isomer is smaller (k_H/k_D = 1.16). This shows that a linear VC with a positive charge on the α-carbon atom is formed from the *Z*-isomer, while in the case of the *E*-isomer the positive charge on the VCI is to a large extent delocalised over the benzene ring, which leads to a lower value of the isotope effect. This example clearly demonstrates that, depending on the configuration of the arylvinyl compounds, the latter can react with or without the involvement of the β-phenyl group.

On passing from the α-alkyl- to the α-aryl-vinyl systems, the stabilising effect of the α-aryl group on the vinyl cationoid centre produced exerts a significant influence on the mode of reaction; this leads to reactions in such systems via open-chain linear VC without the participation of the β-aryl groups. Thus the kinetics, stereochemistry, and degree of the rearrangement in the reactions of the vinyl bromides (LXXVII) and (LXXVIII) clearly show that the β-aryl groups are not involved in the heterolysis of the bonds [59]:



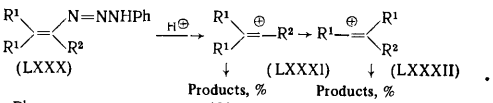
Linear VC are formed analogously from α-anisyl-substituted systems [60]. Numerous data on the solvolysis of β-arylthiovinyl derivatives have shown that the heterolysis of their

bonds proceeds with participation of the β-substituents and with the intermediate formation of thi-irenium ions of the type of (LXXIX).[61]

The degree of the rearrangement caused by the 1,2-shift of the aryl groups via the double bond depends on many factors: the structure of the initial vinyl compound, the method of generation of the VC, the solvents employed, and the nature of the migrating group.

The most significant properties of the solvents for the rearrangements are their nucleophilicity and ionising capacity. It has been suggested[60] that, in solvents with a high dielectric constant, the stability and lifetime of the carbonium ions increase. In highly nucleophilic solvents the rate of reaction of carbonium ions with the solvent increases and there is a corresponding decrease of the yield of rearrangement products. For all the migrations of aryl groups investigated, the best solvent promoting the rearrangements proved to be TFE, which has a high ionising capacity and a low nucleophilicity. In 60% ethanol, which has a higher dielectric constant and is more nucleophilic, the yield of rearrangement products is much lower. Acetic acid occupies an intermediate place between the above solvents. All the remaining factors influencing the degree of rearrangement are to some extent related. However, the decisive factors are of course the structure and stereochemistry of the initial vinyl derivative, because the ease of formation of the VCI in solvolysis, its stability, and hence the tendency towards rearrangements or reactions with the solvent depend on them.

The same VCI can arise in different reactions—in the solvolysis of arylvinyl bromides and arylvinyl triflates and in the interaction of arylvinyltriazenes with acids. Comparative studies[62,63] have shown that in certain cases the degree of the rearrangement depends significantly on the source of the VCI. For example, the solvolysis of the triflate $(Ph)_2C{=}C(OTf)Me$ in 80% EtOH leads to the formation of rearrangement products, while the triflate $(Ph)_2C{=}CHOTf$ is solvolysed very slowly and the rearrangement products are not formed[30]. Formally, the same VC can be generated via the reaction of arylvinyltriazenes (LXXX) with an acid; data on these reactions are compiled below[62,63] (Scheme 1)



(LXXX) → (LXXXI) ↓ (LXXXII)

	Products, %	Products, %
(a) $R^1 = R^2 = Ph$	100	0
(b) $R^1 = n\text{-}MeC_6H_4$, $R^2 = Ph$	80	20
(c) R^1 Ph, $R^2 = Me$	5	86
(d) $R^1 = Ph$, $R^2 = H$	0	90
(e) $R^1 = R^2 = p\text{-}MeOC_6H_4$	68	38

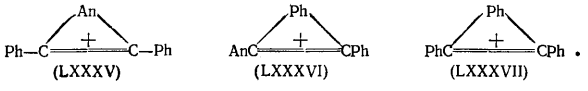
The degree of the rearrangement in symmetrically substituted triazenes (LXXX, a and e) was determined[64] in compounds labelled with ^{13}C or ^{14}C as the vinyl carbon atoms. It is seen from the results presented that the VC (LXXXIc), generated both by the solvolysis of the triflate and by the reaction of a triazene with an acid, rearranges almost wholely to the VC (LXXXIIc). In contrast to these results, the VC (LXXXId) formed in the reaction of triazene also rearranges wholely, but no rearrangement products were detected in the solvolysis of the triflate. This difference in the course of the reaction can apparently be accounted for by the impossibility of the formation of the primary VCI (LXXXId) under the conditions of the solvolysis reaction, as a result of which the solvolysis proceeds via an elimination–addition mechanism.

Other examples indicating the dependence of the degree of rearrangement on the mode of generation of the VC have been obtained in the study of degenerate rearrangements in the VC (LXXXI, a and e) (in systems with labelled vinyl carbon atoms). The reaction of the triazene (LXXXe) with acetic acid results in the formation of 38% of the rearranged acetate. The reaction of trianisylvinyl bromide with silver acetate in acetic acid leads to the formation of 20% of rearrangement products[64], i.e. the yield of the latter diminishes. In contrast to this, the triazene (LXXXa) does not give rise to rearrangement products, while the solvolysis of triphenyl triflate in acetic acid[65] or the interaction of triphenylvinyl bromide with silver acetate in acetic acid[67] lead to the formation of 7% of rearrangement products, i.e. under solvolytic conditions a higher degree of rearrangement is observed. These results can be explained by the different degrees of involvement of the ion pairs in the reaction; whereas in the first instance (the trianisylvinyl cation) the rearrangement proceeds in the VCI formation stage, the formation of rearranged products in the solvolysis of triphenylvinyl compounds takes place in the ion-pair formation stage.

The available data on the solvolysis of various triarylvinyl compounds[60] make it possible to consider the problem of the relative migratory capacities[23] of aryl groups, particularly phenyl and anisyl groups, in rearrangements via the double bond. In this respect one of the most interesting examples is the solvolysis of 2-anisyl-1,2-diphenylvinyl bromides (LXXXIII), since in the resulting VC (LXXXIV) there is a possibility of a 1,2-shift of the phenyl group and of a degenerate rearrangement associated with the migration of the anisyl group (the degree of rearrangement was determined in the solvolysis of 2-anisyl-2-pentadeuterophenyl-1-phenylvinyl bromides[67]):

$$\underset{\text{(LXXXIII)}}{Ph\,(p\text{-}MeOC_6H_4)\,C{=}C\,(Ph)\,Br} \rightarrow \underset{\text{(LXXXIV)}}{Ph\,(p\text{-}MeOC_6H_4)\,C{=}\overset{\oplus}{C}\,(Ph)} \xrightarrow{\sim 1,2\,Ph} p\text{-}MeOC_6H_4\overset{\oplus}{C}{=}C\,(Ph)_2 .$$

The migratory capacity of the anisyl group relative to that of the phenyl group, from competing migrations in the VC (LXXXIV), proved to be 76 for 60% ethanol and 120 for acetic acid. These data demonstrate the difference between the energies of the transition states for the two rearrangements, since the energies of the ground states are the same. Thus the formation of bridged structures of type (LXXXV) with the anisyl group in the transition state is preferable to the formation of structures of the type (LXXXVI):



(LXXXV) (LXXXVI) (LXXXVII)

This is also indicated by a comparison of the 1,2-shift of the anisyl group described above with the 1,2-shift of the phenyl group in the solvolysis of triphenylvinyl triflate. It has been shown[60] that the migratory capacity of the anisyl group in acetic acid is 82 times greater than that of the phenyl group, i.e. in this instance the anisyl group in the transition state (LXXXV) stabilises the positive charge more effectively than the phenyl group in compound (LXXXVII). The degree and mode of the 1,2-shifts of the aryl groups are significantly influenced also by groups not involved in the migration but are linked directly to the atom from which the migrating group departs and to the atom to which it becomes attached. Under these conditions, the stronger stabilising influence of the anisyl group, compared with the phenyl group, on the carbonium ion centre is most significant.

For all the combinations of the substitution of vinyl atoms by phenyl or anisyl groups investigated in the solvolysis of triarylvinyl derivatives, it has been found that the degree of migration to the α-phenyl-substituted centre ($Ar^3 = Ph$) in VC of the type of (LXXXVIII) is greater than the degree of migration to the α-anisyl-substituted centre ($Ar^3 = p\text{-}MeOC_6H_4$):

$$\underset{\text{(LXXXVIII)}}{Ar^1\,Ar^2\,C{=}\overset{\oplus}{C}Ar^3} .$$

On the other hand, the rearrangements of the α-anisyl-substituted VC with formation of an α-phenyl-substituted VC have not been observed. The rearrangements of VC with Ar^1 or Ar^2 = *p*-$MeOC_6H_4$, leading to the formation of VC in which one of the substituents is the phenyl group, are also preferable to the corresponding degenerate rearrangements. It follows from the examples considered that the following transformation is most favourable:

$$(p\text{-}MeOC_6H_4)_2C{=}\overset{\oplus}{C}Ph \xrightarrow{\sim 1,2\,An} p\text{-}MeOC_6H_4C^{\oplus}{=}C(Ph)C_6H_4OMe\text{-}p\ .$$

On the other hand, the degenerate migration of the phenyl group between two anisyl-substituted centres is least favourable:

$$An^*(Ph)C{=}\overset{\oplus}{C}An \rightarrow An^*\overset{\oplus}{C}{=}C(An)Ph\ ;\quad An = p\text{-}MeOC_6H_4\ .$$

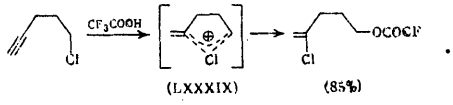
Comparison of the relative capacities for 1,2-migration of the phenyl and anisyl groups in saturated and unsaturated systems[23] shows that in both cases the anisyl group migrates more readily. The only exception has been found in the case of the deamination of 1,2,2-triarylethylamines[68], where a smaller degree of migration was observed for the β-anisyl group compared with the β-phenyl group. In the analogous transformations of phenyltriazenes in reactions with acids, the greater relative migratory capacity of the anisyl group was observed as usual.

IV. HIGHER-ORDER SHIFTS IN VINYL CATIONS

An extremely limited number of examples of such transformations in VCI are available and apparently, as in the case of the "usual" carbonium ions[69], the higher-order shifts are not characteristic of the VCI. In particular, it has been observed earlier that, instead of the 1,3-shift, two consecutive 1,2-migrations of the methyl group take place in the VC (L).[48] Depending on the nature of the migrating group, all the examples of the higher-order shifts described can be divided into two groups: (1) halogen shifts and (2) hydride ion shifts.

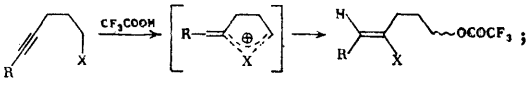
1. The Halogen Shifts

An unusal rearrangement with a 1,4-shift of chlorine in a VC was observed for the first time by Peterson and coworkers[70,71]. They obtained 2-chloropent-4-enyl trifluoroacetate by the reaction of 5-chloropentyne with trifluoroacetic acid. It is apparently formed via a mechanism involving the synchronous protonation of the triple bond and a shift of the halogen via an intermediate state of the chloronium ion type (LXXXIX) with subsequent attack by CF_3CO_2H:



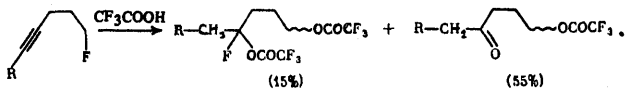
(LXXXIX) (85%)

Interestingly, in contrast to the acetylene derivative, 5-chloropentene gives only 0.6% of the product involving the migration of chlorine. This can be explained by the different degrees of formation of the chloronium ions. It was shown later[72] that the interaction of other halogen-containing acetylene derivatives with analogous structures (5-bromo- and 5-iodo-pentynes, 6-chloro- and 6-iodo-hex-2-ynes) with trifluoroacetic acid also involves a 1,4-shift of the halogen atom:



X = Cl, Br or I.

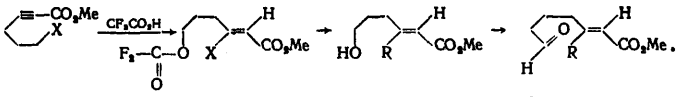
Next it was observed[72] that the interaction of γ-fluoroalkynes with trifluoroacetic acid results in the formation, together with rearranged products, of 15% of a bisadduct corresponding to the fairly unusual 1,4-shift of the fluorine in the VC (similar shifts have not been observed in the chemistry of the "usual" carbonium ions):



(15%) (55%)

The structure of the products obtained shows that exclusive *trans*-addition of the proton and halogen to the triple bond takes place[72].

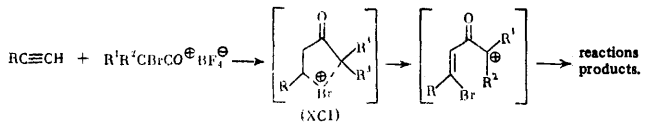
This stereospecific mode of the rearrangement has been used[73] to obtain the aldehyde (XC), which serves as an intermediate in the synthesis of the juvenile hormone:



(XC)

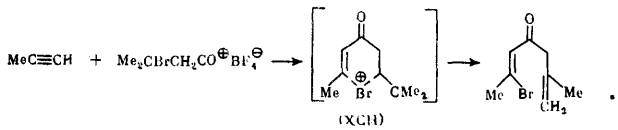
It was found that in the methyl ester of 6-iodohex-2-ynoic acid the 1,4-shift of iodine takes place quantitatively on refluxing for 50 h with trifluoroacetic acid. In contrast to this, the 6-chloroderivative rearranges much more slowly and, after heating the reaction mixture for eight days at 130 °C, only 30% of the rearranged ester and 60–65% of the initial ester were isolated. Thus the esters of acetylenecarboxylic acids rearrange at much lower rates than the alkylacetylenes described above, which is probably associated with the deactivating effect of the methoxycarbonyl group.

The migration of the bromine atom has also been observed in the acylation of alkynes by bromoacylium cationoid reagents[74,75]. In this case the reaction evidently proceeds as the coupled *cis*-addition of the acylium cation and the halide anion to the triple bond. A characteristic feature of the reaction is that the source of the bromide anion is the acylium residue and the final result of the process is a 1,4-shift of the bromine atom. The structure of the final products suggests that in these reactions there apparently arises an intermediate of the type of the five-membered bromonium ion (XCI), the opening of the ring of which actually leads to the formation of β-bromovinyl ketones with a Z-configuration of the double bond:



(XCI)

The interaction of alkynes with β-bromoisovaleryl tetrafluoroborate also leads to the formation of β-bromovinyl ketones[76]. Apparently in this instance a six-membered bromonium ion (XCII) is formed as an intermediate:



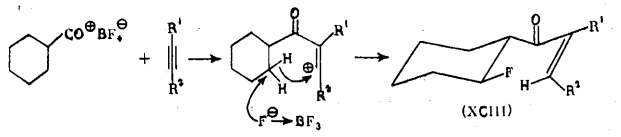
(XCII)

2. The Shift of the Hydride Ion

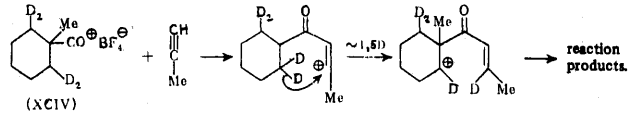
Higher-order hydride shifts constitute a fairly rare phenomenon in the thoroughly investigated chemistry of the "usual" carbonium ions, *trans*-annular reactions involving

rings of medium size constituting an exception[69]. Direct and quantitative data on the 1,3-, 1,4-, and 1,5-hydride shifts are available only for 2,4-dimethyl-2-pentyl, 2,5-dimethyl-2-hexyl-, and 2,6-dimethyl-2-heptyl cations[77]. Here it is of interest to note that the lowest activation energy (25–29 kJ mol^{-1}) is required for the 1,5-hydride shift. The recently discovered new intramolecular 1,5-hydride shift reaction involving VCI is of undoubted interest in this connection.

In the acylation of alkynes with cyclohexanoyl tetrafluoroborate[78], fluoroketones of the type of compound (XCIII) were obtained as the main products:

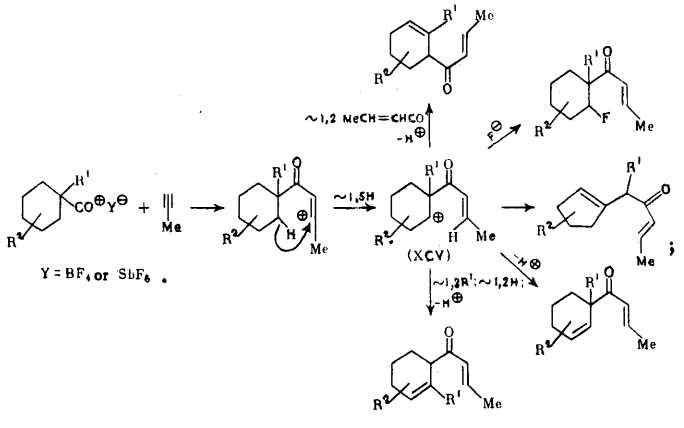


The structure of these compounds (the *E*-configuration of the double bond) suggested that they are formed via an intramolecular 1,5-hydride shift. To demonstrate this hypothesis, Kanishchev et al.[79] used as the acylating agent 1-methyl-2,2,6,6-tetradeuterocyclohexanoyl tetrafluorborate (XCIV):

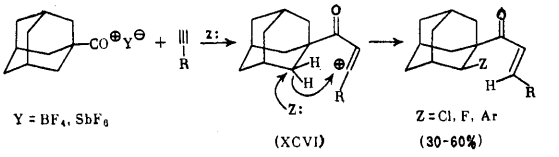


A careful study of the ^{1}H NMR and mass spectra of the reaction products showed that at the β-carbon atom of the side chain there is only a deuterium atom (>95%) and they are therefore formed exclusively via an intramolecular 1,5-hydride shift. It is of interest to note that the hydrogen atoms of the C–H σ-bond of the CH_3 group of the cyclohexane ring do not participate in this reaction; this has also been demonstrated by an experiment in which the protons of the methyl group were replaced by deuterium.

Further study of the acylation of alkynes showed[81–84] that the observed 1,5-hydride shift is a common process in these reactions when aliphatic cycloacylium salts are used as acylating agents. It has been found that this type of transformation takes place most readily for the equatorial position of the carbonyl group in the cyclohexane ring of the initial reactant. A direct result of the 1,5-hydride shift under consideration is the formation of an aliphatic cyclocarbonium ion (XCV); the nature of the final reaction products is determined by the specific features of the structure and stereochemistry of the cyclic skeleton and also by the nature of the nucleophiles present in the medium. In a general form the list of processes observed in these reactions can be represented schematically as follows:



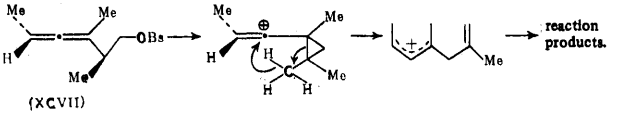
The 1,5-hydride shift takes place particularly effectively in the acylation of alkynes by acylium salts derived from adamantane-1-carboxylic acid[81–84] because in this case the VC (XCVI) formed has six equivalent C–H σ-bonds involving the β-carbon atoms:



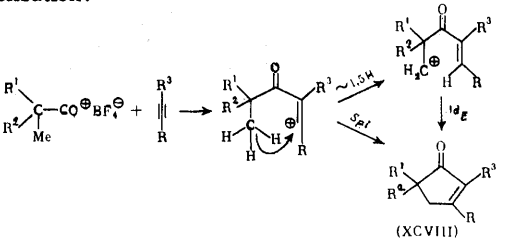
It is readily seen that in all cases the outcome of the reaction is the introduction of a functional group into the aliphatic cyclic residue. The preparative usefulness of these reactions was demonstrated for the formation of a series of 1,2-disubstituted adamantanes, which are difficult to obtain.

Only in the examples of the 1,5-hydride shift described above were the transformations of VCI of this kind rigorously demonstrated. In all other cases the occurrence of higher-order hydride shifts is one of the postulated pathways followed in the transformations of the VC into the final reaction products. For example, in the protonation of branched alkylacetylenes[25] in superacid media the authors do not rule out the possibility of a 1,5-hydride shift in the VC formed, although there are other possible reaction pathways.

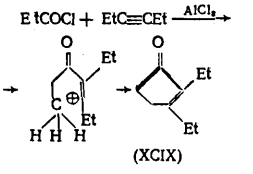
The 1,4-hydride shift has been postulated[85] to account for the formation of nonatrienes in the solvolysis of 2,2,3-trimethylhexa-3,4-dienylbromobenzenesulphonates (XCVII):



In contrast to the acylation of alkynes by aliphatic cycloacylium salts described above, the analogous reactions with cationoid reagents derived from branched aliphatic acids lead to alkylcyclopentenones (XCVII).[86] They are formed via the attack on the β-CH bond of the acylating agent by the cationoid centre, ring closure occurring either via a mechanism involving direct electrophilic substitution (S_Ei) or via a stage in which there is a 1,5-hydride shift with subsequent Ad_E cyclisation:



2,3-Diethylcyclopent-2-enone (XCIX) is apparently formed via an analogous mechanism (in small amounts) in the acylation of hex-3-yne with propionyl chloride[87]:



---oOo---

The data examined above show that sextet rearrangements are just as characteristic of VC as of carbonium ions of other types. The features of VC rearrangements have now been systematically investigated only for the 1,2-migrations of aryl groups. In the majority of cases the result of the investigation has been merely the demonstration of the occurrence of the rearrangement and the elucidation of the general structural features determining its feasibility. There are not yet experimental data characterising quantitatively VC rearrangements. At the same time, the available results show that the transformations of VC are not only of theoretical interest but can also be used for synthetic purposes. An example of useful synthetic processes of this kind is provided by cyclisation (the formation of cyclopentenones), the 1,4-shift of the halogen in the series of ω-halogenoalkynes, the 1,5-hydride shifts in the acylation of alkynes, and finally the generation of allyl cations from alkynes.

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Advances in the Chemistry of α,α'-Disubstituted Pyridines

L.N.Yakhontov and D.M.Krasnokutskaya

The methods of synthesis of α,α'-disubstituted pyridines are surveyed and recent advances in this field are indicated. Various ways of constructing the α,α'-disubstituted pyridine ring and of replacing one set of α,α'-substituents by another are described. The characteristics of the chemical behaviour of α,α'-disubstituted pyridines due to the steric and inductive effects of the substituents and their influence on the reactivity of the nitrogen atom and processes involving electrophilic substitution in the pyridine ring are examined. The chemical behaviour of the various functional groups in pyridine systems with α,α'-substituents as well as the characteristic features of the tautomerism and the dual reactivity of substances of this class are discussed.
The bibliography includes 254 references.

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I. INTRODUCTION

The introduction of α,α'-substituents into nitrogen-containing heteroaromatic compounds alters significantly their chemical properties. Together with the usual inductive and mesomeric effects of the substituents in aromatic systems, their influence on the ring heteroatom is in this case manifested and frequently becomes of primary importance.

The mechanism of this influence has been by no means completely investigated and according to many authors is not restricted to steric and inductive factors but includes additional effects characterised by different investigators as "effects of the proximity to the heteroatom", "the effect of the mutual influence of atoms transmitted through space and not through bonds", "the field effect", etc. The physical significance of these effects is not adequately clear but in one way or another the nature of the heterocyclic nitrogen atom changes markedly under the influence of α,α'-substituents. In many cases its nucleophilic properties and its capacity for protonation, complex formation, and solvation are significantly suppressed. This frequently leads to the loss of specificity in the chemical behaviour of the compounds as nitrogen heterocycles and to the appearance of properties typical for aromatic systems without a heteroatom.

It is noteworthy that the effects of α,α'-substituents in various chemical reactions can be extremely varied. These include the destabilisation of the intermediate carbanions, the ease of chelate formation with the interacting reagents, the suppression of processes proceeding via "conjugate acids", etc. The nature of the mutual influence of the α- and α'-substituents transmitted through the ring heteroatom is complex and to a large extent still remains uninvestigated.

So far as we are aware, there are no reviews in the literature dealing with the influence of α,α'-substituents on the properties of azine systems. The aim of the present review is an attempt to fill this gap to some extent and to survey the available information for the simplest case of α,α'-disubstituted nitrogen-containing heterocycles, namely α,α'-disubstituted pyridines. The review surveys also the methods of synthesis of α,α'-disubstituted pyridines described in numerous scattered articles and reviews devoted to specific problems and the advances achieved in this field in recent years.

II. METHODS OF SYNTHESIS OF α,α'-DISUBSTITUTED PYRIDINES

α,α'-Disubstituted pyridines can be obtained by various methods:

(1) By constructing the pyridine ring from aliphatic compounds.

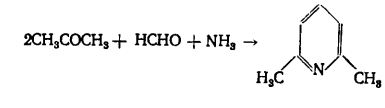
(2) By converting a wide variety of cyclic non-pyridine compounds into α,α'-disubstituted pyridines.

(3) By replacing one set of substituents in α,α'-disubstituted pyridines by another.

The methods of synthesis of new compounds involving a change in the nature of the substituents only in the β-, β'-, or γ-positions of the pyridine ring and not involving the α,α'-substituents constitute a special group, which will not be discussed in this review.

1. Synthesis of α,α'-Disubstituted Pyridines from Aliphatic Compounds

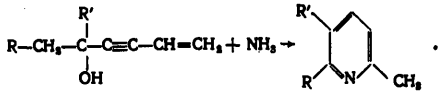
The classical method of synthesising α,α'-disubstituted pyridines with alkyl or aryl residues is the Chichibabin reaction, widely used in the pyridine chemistry and based on the condensation (usually in the gase phase) of ammonia with ketones, aldehydes, nitriles, acetylene derivatives, or their mixtures[1,2]. A series of 2,4,6-triarylpyridines have been synthesised by this method from aromatic aldehydes, aryl methyl ketones, and ammonium acetate[3]. The Chichibabin reaction is used also on an industrial scale to obtain synthetic 2,6-dimethylpyridine (2,6-lutidine) via the mechanism[4]



The synthesis of α,α'-dialkylpyridines by the interaction of aliphatic ketones with ammonia in the gas phase on a platinum catalyst has been recently reported[5].

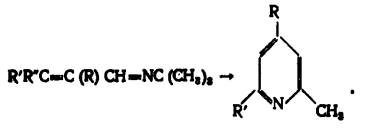
A number of 6-alkyl(aryl)-2-methylpyridines have been obtained by the condensation of vinylacetylenic alcohols

with ammonia[1]:

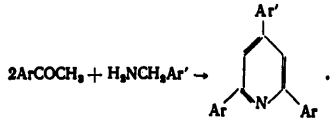


A mixture of the corresponding ketone with vinylacetylene can also be used in the reaction with ammonia.

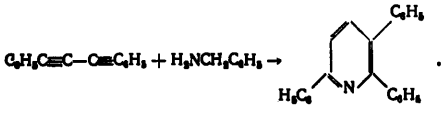
The reaction of unsaturated imino-compounds with chromium and aluminium salts has been used to obtain 4-ethyl-2,6-dimethylpyridine and its analogues via the mechanism[6]



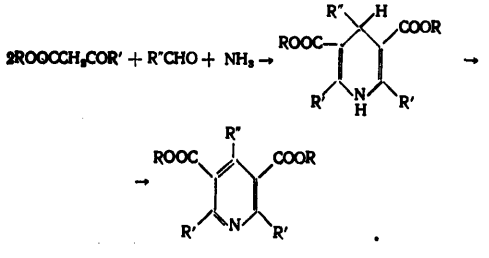
2,4,6-Triarylpyridines are obtained by Reddelin's method involving the condensation of acetophenone with benzylamines in the presence of traces of hydrogen bromide[7,8]:



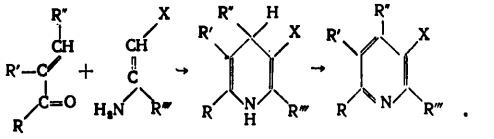
Refluxing of diphenylbutadiyne with benzylamine leads to 2,3,6-triphenylpyridine[9]:



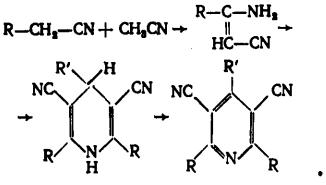
The Hantzsch reaction[10], involving the cyclocondensation of β-ketoesters with aldehydes and ammonia and subsequent oxidation of the 1,4-dihydropyridine derivatives formed, is of practical importance in the synthesis of α,α'-disubstituted pyridines:



Many modifications of Hantzsch's method are known. Instead of ammonia, ammonium acetate, formamide, urotropine, and more rarely primary amines are introduced into the reaction. Together with acetoacetic esters, the esters of cyanoacetic and malonic acids and their various derivatives are used as the carbonyl components: enol acetals, enol esters, iminoethers, etc. In many instances, particularly in the synthesis of asymmetric compounds, it is convenient to begin with α,β-unsaturated ketones, which are intermediates in the Hantzsch reaction formed on condensation of aldehydes with β-dicarbonyl compounds or from substances of analogous structure: methylene aldehydes, methylene ketimines and esters, acetylenic amidines[11], β-chlorovinyl ketones[12], etc. Another possible intermediate in the Hantzsch synthesis—β-aminocrotonic ester or substance of analogous structure (enaminoketones, enaminonitriles, etc.)—are frequently used as second components in these reactions[10,11]:

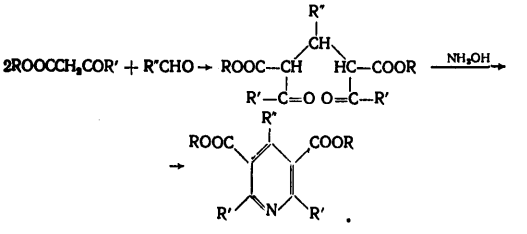


One of the variants of the Hantzsch synthesis is the Meyer–Mohr reaction[13], involving the cyclocondensation of aldehydes or ketones with enaminonitriles obtained on interaction of various nitriles with acetonitrile in the presence of strong bases:



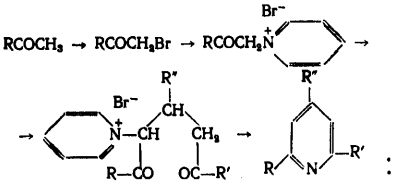
Another variant consists of the condensation of β-aminocrotonic ester with 1,3-enynylamines[14], sodioformylacetone, the acetal of ethoxycrotonaldehyde, or α-ethynylcarbonyl compounds[15].

The isolation of the intermediate product of the condensation of acetoacetic ester with an aldehyde (a derivatives of a 1,5-diketone) and its treatment with hydroxylamine constitute a modification of the initial Hantzsch synthesis[253]:

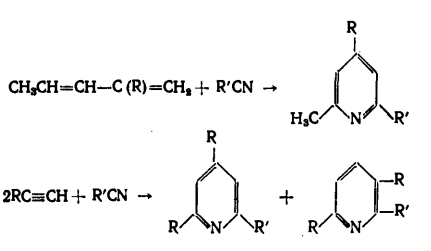


The direct cyclisation of 1,5-diketones and their oximes or imines has also been described[1,11,16].

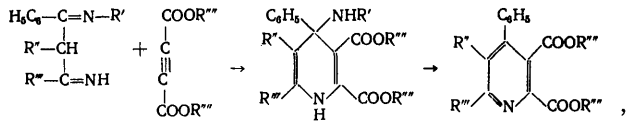
The synthesis of α,α'-disubstituted pyridines from *N*-acetonylpyridinium salts, unsaturated ketones, and ammonium acetate via 1,5-dicarbonyl compounds, proposed by Kröhnke,[17,18] is of considerable preparative interest:



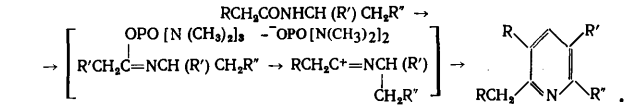
Certain α,α'-disubstituted pyridines have also been obtained by the reaction of nitriles with dienes[19] or acetylenes[20]:



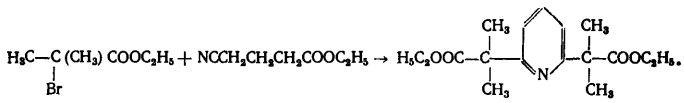
or of 1,3-di-imines with acetylenedicarboxylate esters[21]:



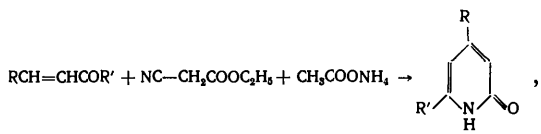
by the cyclisation of secondary carboxamides involving cautious heating in hexamethylphosphoramide[22]:



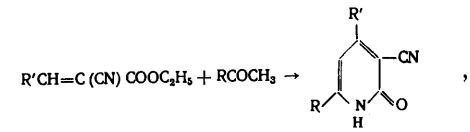
or by the condensation of α-bromoesters with γ-alkoxycarbonylnitriles under the conditions of the Reformatzky reaction[23]:



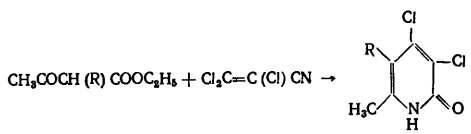
A method of synthesis of 6-substituted 2-pyridones, which follows directly from the Hantzsch reaction, is based on the condensation of the derivatives of malonic ester or malononitrile with enamines[24-28] and also of cyanoacetic ester with α,β-unsaturated ketones and aminoacetate[29]:



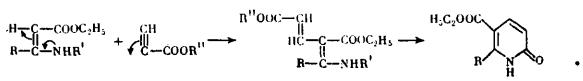
of cyanoacrylic esters with ketones[30]:



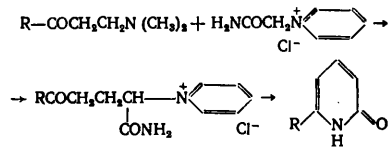
or of β-ketoesters with trichloroacrylonitrile[31]:



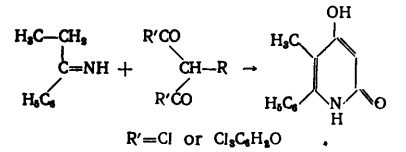
When enaminoesters react with propiolic acid esters, dienamines, which are also capable of cyclising to 6-substituted 2-pyridones, are formed readily[32]:



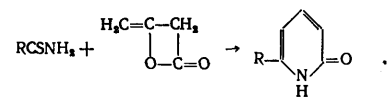
The condensation of α,β-unsaturated ketones or the corresponding products of the Mannich reaction with *N*-carbamoylmethylpyridinium salts also leads to 6-substituted 2-pyridones[33]:



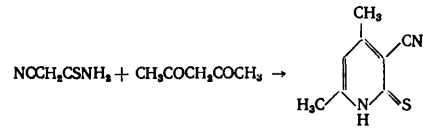
The 2-pyridones are likewise obtained when propiophenoneimine interacts with monosubstituted malonyl chlorides[34] or malonic esters[35]:



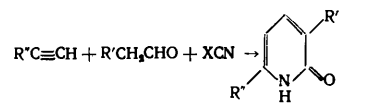
Another way of synthesising 6-substituted 2-pyridones containing in addition a hydroxy-group in the 4-position consists in the condensation of thioamides with diketen[36]:



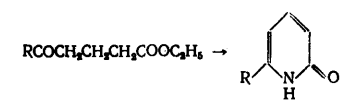
The cyclocondensation of cyanothioacetamide with acetylacetone yielded 3-cyano-4,6-dimethyl-2-pyridinethione:



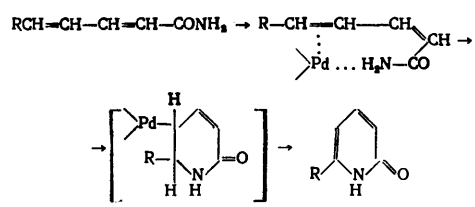
while the condensation of acetylenic compounds with aldehydes and nitriles gave rise to 3,6-disubstituted 2-pyridones[37]:



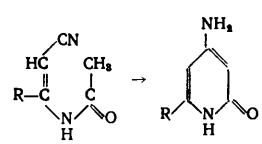
By analogy with the cyclisation of 1,5-diketones discussed above, the interaction of 5-oxoalkenecarboxylic acids or their derivatives (amines, nitriles, etc.) with ammonia or primary amines also leads to the formation of 2,6-disubstituted pyridines—in the given instance 6-substituted 2-pyridones[11]:



The methods of synthesis of 6-substituted 2-pyridones by the cyclisation of 2,4-pentadienamides with lithium chloropalladate(II) in acetonitrile in the presence of triethylamine[38], i.e.

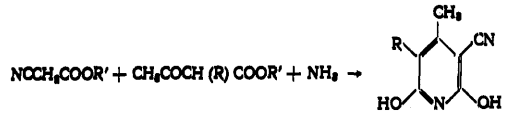


and the Dieckmann cyclisation of certain *N*-substituted amides via the mechanism[11]



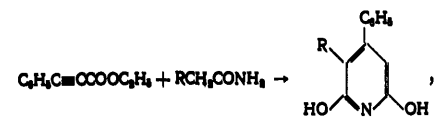
occupy a special place.

The most general and most widely used method of synthesis of α,α'-dihydroxypyridines is the Guareschi–Thorpe reaction[11,39,40], which is based on the cyclocondensation of cyanoacetic and α-alkylacetoacetic esters with ammonia:

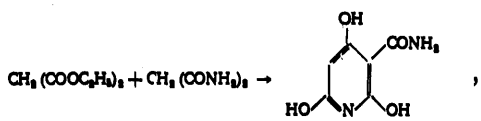


The corresponding amides are frequently used in this reaction instead of esters. The alkyl substituent R may contain different functional groups and multiple bonds. The cyclocondensation is usually carried out in water at room temperature, but reactions without a solvent or in non-aqueous media have also been described[39]. α,β-Unsaturated carbonyl compounds have been used instead of acetoacetic ester or amide[11]. Cyclocondensation with cyanoacetic ester or cyanoacetamide is carried out in this case in the presence of alkali metal alkoxides. One of the variants of the synthesis involves the interaction of cyanoacetic ester with aldehydes and ammonia, whereupon α,β-unsaturated carbonyl derivatives are formed as intermediates as a result of the reaction of the aldehydes with cyanoacetic ester.

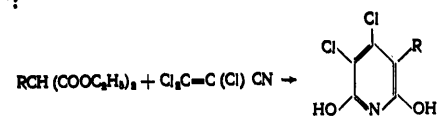
The cyclocondensation of phenylpropiolic ester with amides leads to 3,4-disubstituted 2,6-dihydroxypyridines[41,42]:



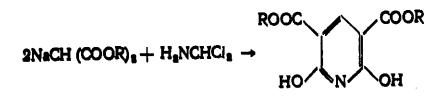
that of malonic ester with malonodiamide in the presence of sodium methoxide produces 3-carbamoyl-2,4,6-trihydroxypyridine[43]:



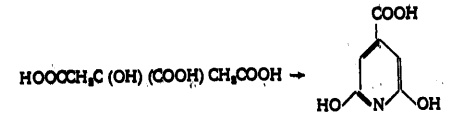
and that of substituted malonic ester with trichloroacrylonitrile under the influence of potassium t-butoxide results in the formation of 3-substituted 4,5-dichloro-2,6-dihydroxypyridines[44]:



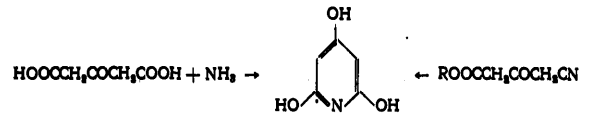
The Gattermann–Skitta reaction, involving the formation of 2,6-dihydroxypyridines by the cyclocondensation of sodiomalonic ester with dichloromethylamine, is a variant of the Hantzsch synthesis[254]:



Different variants of the cyclisation of glutaric acid and its substituted derivatives are widely used for the synthesis of α,α'-dihydroxypyridines. β-Oxo-, β-hydroxy-, and β-imino-derivatives of glutaric acid as well as substituted β-carboxy-β-hydroxyglutaric (citric) acid are most often used for this purpose[11]. An example is provided by the synthesis of 2,6-dihydroxyisonicotinic (citrazinic) acid from citric acid and its conversion into isonicotinic acid (the method has found industrial application)[45]:

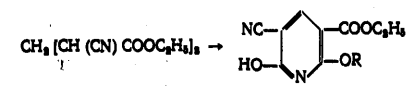


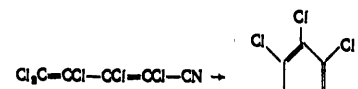
as well as the cyclisation with ammonia of β-oxoglutaric (acetonedicarboxylic) acid, its esters, or mononitrile[11]:

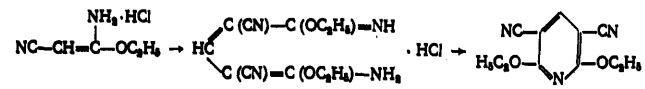


Aryl isothiocyanates or aryl isocyanates have also been used as nitrogen-containing components in these reactions[46].

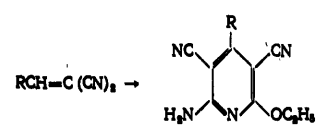
The reactions of methylenebiscyanoacetic esters[11] and pentachloropentadienonitrile[47] with alkali metal oxides as well as the interaction of acid α-methylene derivatives with symmetrical triazine[48] have been used for the closure of a pyridine ring containing 2-alkoxy-6-hydroxy(alkoxy) substituents:





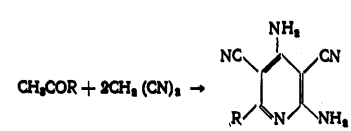


The most general method of synthesis of 2-alkoxy-6-aminopyridines, based on the closure of the pyridine ring, is the condensation of substituted methylenemalonodinitriles with alkali metal alkoxides[49–52]:

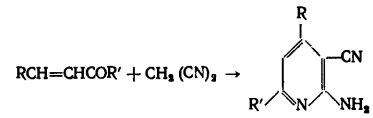


The reactions of acetoacetic or malonic esters with methylene amidines, methyleneimidates, and 5-aminopyrazolones[53], the cyclisation of acetonedicarboxylic ester with ammonia[54], and the condensation of acetylenic compounds with cyanamide[20] are used for these purposes.

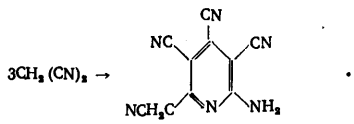
Malonodinitrile has been widely used in recent years in the synthesis of 6-substituted 2-aminopyridines[55]; the condensation of the dinitrile with methyl ketones in the presence of an excess of ammonium acetate leads to 6-alkyl-2-aminopyridines[56,57]:



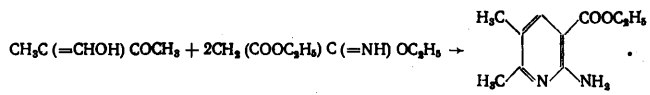
The reaction with unsaturated ketones proceeds in a somewhat different manner[56] via the mechanism



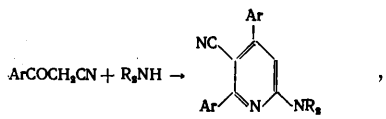
Under the influence of zinc chloride, malonodinitrile trimerises[55]:



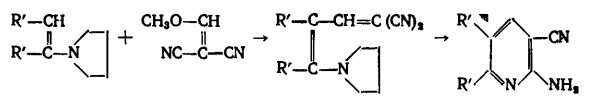
Substituted 2-amino-6-methylpyridine has been obtained by the condensation of ethyl α-hydroxymethylenemethyl ketone with monoiminomalonic ester[58]:



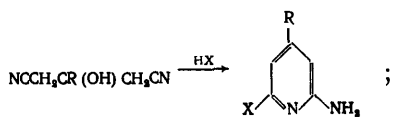
The analogous 6-aryl derivatives are formed on condensation of ω-cyanoacetophenones with secondary amines[59]:



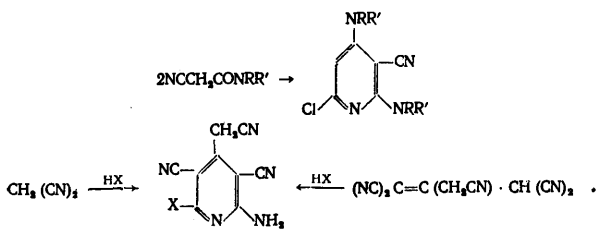
while 6-alkyl derivatives are formed when enamines interact with methoxymethylenemalonodinitrile via intermediate dienamines[60]:



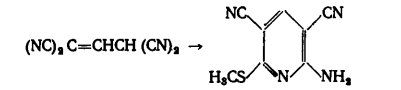
The reactions of 3-hydroxyglutarodinitrile with primary and secondary amines lead to substituted α,α'-diaminopyridines[61]. The use of anhydrous hydrogen bromide or iodide in analogous processes makes it possible to obtain high yields of 2-amino-6-halogenopyridines[62,63]:



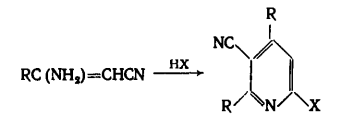
Both possible 2,6-disubstituted isomers are obtained from asymmetric starting materials[64]. Instead of the hydroxy-derivative, the corresponding unsaturated dinitrile can be used in the reaction[65]. Substituted 2-amino-6-chloropyridines have been obtained by the interaction of cyanoacetyldialkylamines with phosphoryl chloride[66] and also by treating malonodinitrile[67], 1,1,3,3-tetracyanopropene, or 2-cyanomethyl-1,1,3,3-tetracyanopropene[63] with hydrogen halides:



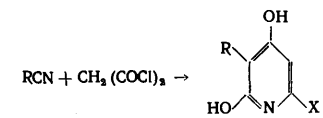
The condensation of 1,1,3,3-tetracyanopropene with methylisothiourea leads to substituted 2-amino-6-methylthiopyridine[68]:



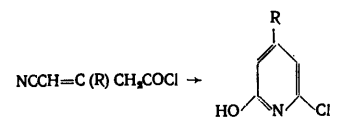
The interaction of enamines with methoxymethylenemalonodinitrile and treatment of the intermediate dienamines with hydrogen halides instead of ammonia made it possible to obtain 6-substituted 2-halogenopyridines[60]. Analogous compounds are also formed on cyclisation of the nitriles or esters of 6-aminocinnamic and β-aminocrotonic acids in the presence of hydrogen halides[70,71]:



2-Halogeno-6-hydroxypyridines have been synthesised by the condensation of malonyl chloride with nitriles[71]:

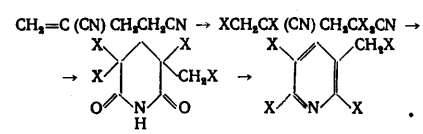


Another method of synthesising compounds of this type consists in the cyclisation of the chlorides of unsaturated γ-cyanoacids under the influence of hydrogen halides[72]:



6-Alkoxy-2-halogenopyridines are formed on cyclisation of perchloropentadienonitrile under the influence of a Grignard reagent[73].

The reaction of glutaramides and glutarimides with phosphorus halides and subsequent aromatisation of the cyclic halogeno-derivatives[74,75] as well as the dimerisation of acrylonitrile, the halogenation of the dimer, the cyclisation of the product, and treatment of the substituted glutarimide with phosphoric acid halides[76] have been used to obtain 2,6-dihalogenopyridines:

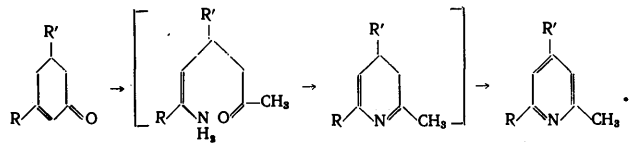


2. The Synthesis of α,α'-Disubstituted Pyridines from Other Cyclic Compounds

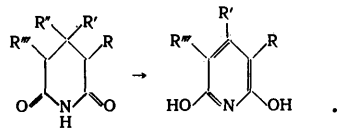
Methods based on the conversion of various non-pyridine cyclic systems into pyridine systems have played an important role in the synthesis of α,α'-disubstituted pyridines.

6-Substituted 2-methylpyridines have been obtained[77] in low yields by heating cyclohexanones with ammonia or ammonium chloride under pressure at 250 °C.[77] It was assumed that the process proceeds via the intermediate formation of

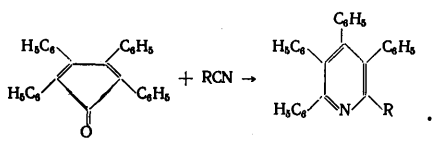
enamines derived from 1,5-dicarbonyl compounds:



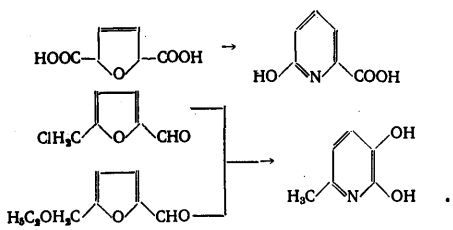
The synthesis of α,α'-dihydroxypyridines (derivatives of glutaconimide) by the oxidation of the corresponding glutarimides has been described[11]:



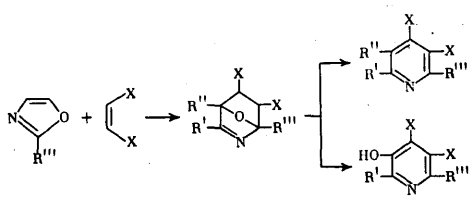
High yields have been achieved in the Diels–Alder condensation of tetraphenylcyclopentadienone with nitriles[78]:



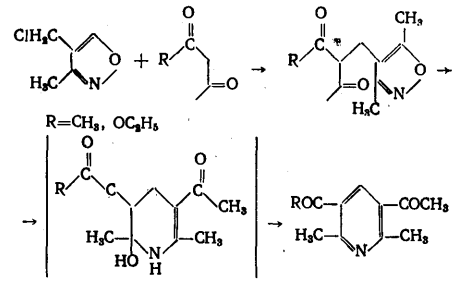
6-Hydroxypicolinic acid has been obtained from 2,5-dicarboxy-2,5-dihydrofuran on heating to 160 °C with aqueous ammonia and ammonium bromide[79]. The reactions of 5-chloromethyl- and 5-ethoxymethyl-furfurals with aqueous ammonium chloride result in the formation under the same conditions of 2,3-dihydroxy-6-methylpyridine together with other products, while 5-substituted 2-acetylfurans are converted into 2,6-disubstituted 3-hydroxypyridines[80–82]:



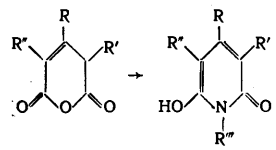
The azadiene condensation of substituted oxazoles with dienophiles (the Kondrat'eva reaction), discovered at the end of the 1950's, constitutes an interesting method of synthesis of α,α'-disubstituted pyridines[83]:



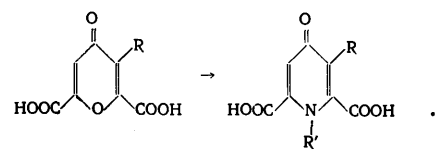
α,α'-Disubstituted pyridines have been synthesised from isoxazoles by catalytic hydrogenation via the mechanism[84,85]



The transformations of the corresponding six-membered oxygen-containing heterocycles occupy a definite place in the synthesis of α,α'-disubstituted pyridines. For example, 6-substituted α-pyrones, obtained by the reaction of malonyl chloride with isocyanates, are converted by treatment with ammonia or amines into the corresponding 6-substituted 2-hydroxypyridines[11,86]. Reactions of this type have been examined in a review[87]:

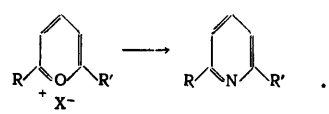


α,α'-Disubstituted γ-pyrones of the type of chelidonic acid are converted into α,α'-disubstituted γ-pyridones (derivatives of chelidamic acid) on treatment with ammonia or amines[88]:

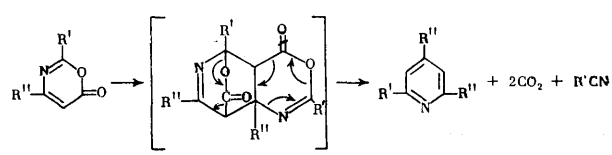


α,α'-Dihalogeno-γ-pyrones give rise similarly to α,α'-dihalogeno-γ-pyridones[89].

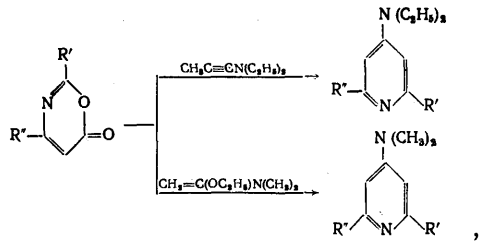
Numerous 2,6-disubstituted pyridines [including 2,6-di(t-butyl)pyridines, which are difficult to obtain by other methods[90]] have been synthesised by the reaction of 2,6-disubstituted pyrylium salts with ammonia or amines[91–93]:



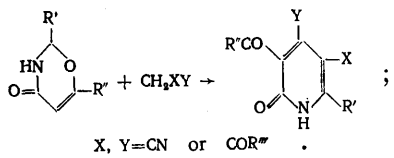
A group of methods is based on the use of oxazine and diazine derivatives as starting materials. These include the pyrolytic cleavage of 6-hydroxy-6*H*-1,3-oxazines[94]:



on interaction with ynamines and keten *O*,*N*-acetals[95]:

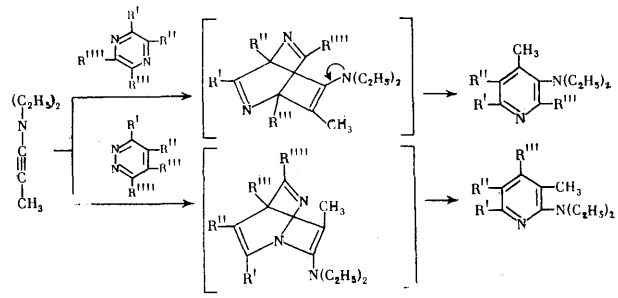


and also the reactions of 2-aryl(alkyl)-4-hydroxy-4*H*-1,3-oxazines with β-dicarbonyl or β-cyanocarbonyl compounds[96]:

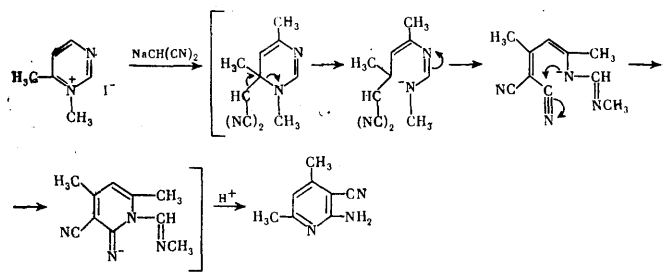


X, Y=CN or COR''' .

The Diels–Alder condensation of 1-diethylaminopropyne with pyrazine[97] and pyridazine[98] derivatives, i.e.



and the rearrangements of 4-substituted pyrimidines and their quaternary derivatives under the influence of nucleophiles[99–101], i.e.



belong to the same group.

3. Methods of Transforming α,α′-Substituents in the Pyriding Ring

Reactions involving the classical transformation of one set of α,α′-substituents in pyridine structures into another occupy an important place in the synthesis of α,α′-disubstituted pyridines[1,11].

2,6-Dihydroxypyridines are obtained by the hydrolysis of 2,6-diamino, 2,6-dihalogeno-, or 2,6-dialkoxy-pyridines; 6-chloro-2-hydroxypyridines are synthesised by the diazotisation of 2-amino-6-chloropyridine and by the hydrolysis of 2,6-dichloro- or 2-alkoxy-6-chloro-pyridines. 2,6-Dialkoxypyridines are synthesised by the reaction of 2,6-dihalogenopyridines with alkali metal alkoxides[102] or by the alkylation of 2,6-dihydroxypyridines[103]. Under milder conditions, 2,6-dihalogenopyridines react with alkali metal alkoxides to form 6-alkoxy-2-halogenopyridines.

2,6-Dihalogenopyridines are obtained by the reaction of the corresponding 2,6-dihydroxy-derivatives with phosphoric acid halides or hydrogen halides, by the direct halogenation of pyridine bases, their *N*-oxides, or carboxylic acids[104,105], by the substitution of one halogen by another on interaction with hydrogen halides or their salts[106,107], by the arrangement of 2-chloropyridine *N*-oxide on interaction with phosphoryl chloride[108], and by the replacement of nitro-groups by a halogen in the reaction with hydrogen halides.

The reactions of various α,α′-disubstituted pyridines with hydroxy- or halogeno-groups as substituents with P_2S_5 yielded α,α′-dimercaptopyridines[109].

2-Amino-6-halogenopyridines have been synthesised from 2,6-dihalogenopyridines by the substitution of one halogen by an amino-group and from 2-amino-6-hydroxypyridine by the substitution of the hydroxy-group by a halogen; 2,6-diaminepyridines have been synthesised by the corresponding reactions of 2,6-dihalogenopyridines or 6-alkoxy-2-chloropyridines, by the direct Chichibabin amination of pyridines[110], or from dipicolinic acid via the Curtius or Hofmann reactions[111].

6-Alkoxy-2-aminopyridines are obtained by substituting the halogen by an amino-group in 6-alkoxy-2-halogenopyridines; 2-amino-6-nitropyridines are synthesised by the substitution of the bromine atom by the amino-group in 2-bromo-6-nitropyridines; 2-amino-6-hydroxypyridines are obtained by the Chichibabin reaction from α-pyridone or by the hydrolysis of 2,6-diaminopyridine. An interesting instance of the direct amination of 3-azido-2-nitropyridine with formation of a 6-amino-2-nitropyridine derivative and of 2,3,6-triaminopyridine from the latter has been described recently[112].

Direct nitration of pyridine in the α,α′-positions with formation of the 2,6-dinitro-derivatives is possible only in the presence of a strong electron-donating substituent such as an alkoxy-group in the β-position[113]. 3-Methoxy (or hydroxy)-6-methylpyridines are converted on nitration into 3-methoxy(or hydroxy)-6-methyl-2-nitropyridines[114]; the nitration of 3-hydroxy-2-nitropyridine leads to 2,6-dinitro- and 3-hydroxy-2,4,6-trinitropyridine[115]. Kinetic studies have shown that the nitration process involves in these instances the protonated form and that the partial nitration rate constants are 4×10^{-10} for the 2-position and 1×10^{-11} for the 6-position in the 3-methoxypyridinium cation[116]. The halogenation of 3-alkoxy(or hydroxy)pyridines leads similarly to 2,6-dihalogeno-derivatives[113,117], aminomethylation gives rise to 3-alkoxy(hydroxy)-2,6-di(aminomethyl)pyridines[113,118,119], and hydroxymethylation leads to 3-alkoxy-2,6-di-(hydroxymethyl)pyridines[113].

The aminomethylation of 3-hydroxypyridines containing alkyl, alkoxy-, hydroxy-, or nitro-groups in the 2-position, takes place in the 6-position[113,120–124] and the hydroxymethylation of 3-hydroxy-6-methylpyridine involves the 2-position [123,125]; 5-hydroxypicolinic acid is converted as a result of an analogous reaction into 5-hydroxy-6-hydroxymethylpicolinic acid[126]. The azo-coupling of 2,3-dihydroxy-3-ethoxy-2-methoxy-, or 2,5-dihydroxy-pyridines involves the 6-position[127].

Methods of synthesis of 2,6-di(hydroxymethyl)pyridine from 2,6-lutidine via 2,6-diformylpyridine[128-130] or its *N*-oxide[131], via 2,6-di(chloromethyl)pyridine[132] and 2,6-dicyanopyridine[133], and also on the basis of the Böckelheide reaction repeated twice[134] or the oxidation of 2,6-lutidine to dipicolinic acid with reduction of the esters of the latter by complex metal hydrides have been recommended[135].

2,6-Di(bromomethyl)pyridine has been obtained from 2,6-di(hydroxymethyl)pyridine[136] and also by the direct radical bromination of 2,6-lutidine[137]. 2,6-Diformyl pyridine has been synthesied by the catalytic oxidation of 2,6-lutidine[128, 130,138]. 6-Formylpicolinic acid has been obtained similarly from 6-methylpicolinic acid[11].

The Claisen condensation of dipicolinic ester with ethyl acetate has been used to synthesise 2,6-diacetylpyridine[139], while 2,6-dibenzoylpyridine has been obtained by the Friedel–Crafts condensation of dipicolinic acid dichloride with benzene[11]. 2,6-Diacylpyridines have been reduced by the Kishner method to 2,6-dialkylpyridines[140].

The reaction of pyridine *N*-oxide with phenylmagnesium bromide gave a low yield of 2,6-diphenylpyridine together with 2-phenylpyridine[11]. The synthesis of 2,6-dicyanopyridine from 2,6-dibromopyridine and copper cyanide has been described[141].

Potassium permanganate[142], selenium dioxide or its complexes[143], nitrogen oxides in the presence of selenium dioxide[144], sodium dichromate and chromic anhydride[145] have been used as oxidants for the conversion of 2,6-lutidine into 6-methylpicolinic and dipicolinic acids. Dipicolinic acid has also been obtained by the carboxylation of pyridine[146] or picolinic acid[147] and by the oxidative ammonolysis of 2,6-lutidine[148,149] with subsequent hydrolysis of 2,6-dicyanopyridine[150].

III. CHEMICAL CHARACTERISTICS OF α,α′-DISUBSTITUTED PYRIDINES

1. The Influence of α,α′-Substituents on the Reactivity of the Nitrogen of the Pyridine Ring

In the complex mechanism of the influence of α,α′-substituents on the pyridine nitrogen atom steric effects, which have been studied in greatest detail in relation to 2,6-dialkylpyridines, play an important role. Brown and coworkers[151-153] and then other investigators[154,155] showed that, when α,α′-methyl groups are introduced, steric hindrance to the protonation of the pyridine nitrogen is not observed. However, on passing to 2,6-di(t-butyl)pyridine, the pK_a and the heats of neutralisation with methanesulphonic acid in nitromethane (ΔH) clearly indicate a significant steric hindrance in the protonation process. In the analogous reaction with picric acid steric hindrance is manifested even in 6-(t-butyl)-2-isopropylpyridine, which, like 2,6-di(t-butyl)pyridine is incapable of forming a picrate.

On passing from protonation to complex formation involving more bulky reagents—the Lewis acids [BH_3, BF_3, and $B(CH_3)_3$]—steric hindrance becomes appreciably more significant. For example, the heats of formation of complexes with BF_3 decrease in the sequence pyridine > α-picoline > 2,6-lutidine by 9.2 and 35.6 kJ mol^{-1} respectively. In the analogous reaction in $B(CH_3)_3$ the value of $\Delta\Delta H$ is 24.7 kJ mol^{-1} even for α-picoline, while 2,6-lutidine does not form a complex with this reagent at all.

The above steric effects are not only of theoretical but also of preparative interest in a number of instances; the methods of separation of 2,6-lutidine from other components of the β-picoline fraction[156] and the methods of separation of protic and Lewis acids[157] are based on them.

Analogous steric effects are observed also in the interaction of α,α′-disubstituted pyridines with alkyl halides. For example, 2,6-di(t-butyl)pyridine does not form a quaternary salt even with methyl iodide. 2,6-Dimethyl-, 2,6-diethyl, and 2,6-di-isopropylpyridines are converted under identical conditions into methiodides in yields of 99, 74, and 45% respectively[140].

α,α′-Functional substituents exert a more complex influence on the heterocyclic nitrogen atom. For example, in the case of 2,6-dihalogenopyridines the substituents exhibit, in addition to a definite steric effect, a much stronger inductive electron-accepting influence[158]. In contrast to compounds without halogen atoms or α-monohalogeno-derivatives[158-160], 2,6-dihalogenopyridines do not form stable salts with inorganic acids, do not give rise to picrates or complexes with Lewis acids[74,158,161], form quaternary salts with very great difficulty even after prolonged heating at high temperatures under pressure, and are virtually not oxidised to N-oxides[158].

In contrast to 6-methylpicolinic acid, dipicolinic (pyridine-2,6-dicarboxylic) acid is a very weak base and, for example, does not combine with cation-exchange resins in the H^+-form. This permits the esterification of dipicolinic acid by various alcohols in the presence of ion exchangers in high yields[135].

2. The Influence of α,α′-Substituents on the Transformations of the Functional Groups in Other Positions in the Pyridine Ring

The change in the basicity of the pyridine nitrogen under the influence of α,α′-substituents influences not only the processes involving the heteroatom but also the reactivity of the entire pyridine system.

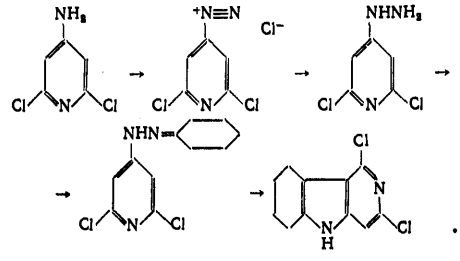
Significant differences between the reactions of pyridines and the analogous benzene derivatives are known to be related both to the change in the distribution of electron densities in the aromatic system owing to the electron-accepting influence of the pyridine nitrogen and to the fact that many electrophilic reactions do not involve the free pyridine bases but take place with participation of the corresponding "conjugate acids", which are characteristed by an even greater electron-accepting effect of the positively charged heteroatom[162,163].

The introduction of α,α′-substituents into the pyridine ring affects both the distribution of electron density in the system and the ease of formation of the corresponding "conjugate acids". The influence of the ring heteroatom is therefore to a large extent blocked in many reactions of pyridines having electron-accepting or sterically hindered substituents in the 2- and 6-positions and compounds of this type begin to behave like the analogous benzene derivatives.

Pyridines are sulphonated with fairly considerable difficulty, forming more readily complexes with SO_3 via the nitrogen atom[11]. 2,6-Di(t-butyl)pyridine, in which the nitrogen heteroatom is sterically hindered and is incapable of forming the "conjugate acid" under the reaction conditions, proved to be capable of being sulphonated in the 3-position under very mild conditions—by reaction with sulphur trioxide in liquid SO_2 below 0 °C.[151,152] In contrast to the corresponding dehalogenated compounds, the γ-methyl group in α,α′-dihalogeno-γ-methylpyridines does not condense with aldehydes and mesoxalic ester and is not oxidised by selenium dioxide even under very severe conditions[158]. The chlorides of 2,6-dihalogenopyridine carboxylic acids readily undergo the Rosenmund reaction to aldehydes[164], like the chlorides of

aromatic acids; the corresponding 2,6-dehalogenated derivatives of pyridine are not converted into aldehydes by this procedure.

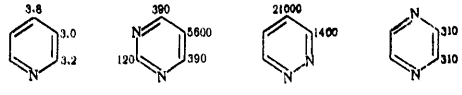
In contrast to the usual 4-aminopyridines, which do not form stable diazonium salts, 4-amino-2,6-dichloropyridine is easily converted on treatment with sodium nitrite into a fairly stable diazonium salt[165], which is reduced in a high yield by tin(II) chloride to 2,6-dichloro-4-pyridylhydrazine. The thermal conversion of the corresponding 4-pyridylhydrazones into indoles in methylene glycol, in which a positively charged pyridinium nitrogen is not formed, actually proceeds with greater difficulty and is less unambiguous for 2,6-dichloropyridines than for the analogous substances without halogen atoms[165]:



Apparently the smaller capacity of α,α'-dihalogenopyridine derivatives for solvation by ethylene glycol has an effect in this instance.

Interesting results were obtained in the study of the quantitative effects of α-substituents by the method of correlation analysis. Determination of a series of such compounds led Zuman[166] to assert that such substances exhibit the "effect of proximity to the heteroatom" with a deviation from the correlation. A study of different series showed that, in contrast to *ortho*-substituted anilines, for α-substituted pyridines the correlation is better in terms of σ_{meta} and σ_{ortho} constants; on this basis, the author[167] concluded that there is virtually no transmission of the influence of α-substituents in terms of the conjugation effect. Owing to the short distances between the α-substituent and the nitrogen, the mutual influence of these reaction centres is exerted through space and not through the bonds. The field effect is taken into account by σ' and σ* constants and less rigorously by the σ_{meta} constant. A field effect decaying rapidly with distance is virtually atypical for the analogous benzene derivatives, where the distance between the reaction centres in the *ortho*-positions is much greater.

For a quantitative estimate of the influence of α-substituents in *N*-heteroaromatic systems, measurements were made[168] of the rate of deuterium isotope exchange in an alkaline medium for different positions of the heterocycles (the rate constants for the exchange of the corresponding hydrogen atoms at 164.6 °C multiplied by a factor of 10^6 are indicated below):



It was found that the hydrogen atoms located near the carbon atoms between the two nitrogen atoms or at the carbon atoms adjoining the nitrogen atoms usually exhibit the smallest capacity for deuterium exchange under these conditions. In pyridine, for example, the base-catalysed deuterium exchange takes place most readily in the 4-position[169], although according to the calculations of charges by the Hückel method the 2-position should be the most "acid"[168].

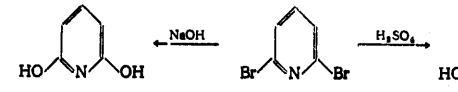
The reduced activity of the α-positions in isotope exchange reactions[170] is apparently the result of the operation of two factors: the decrease of the amount of *s* character of the hydrogen bond with the carbon adjoining the atom of the nucleophile and the repulsion between the electron pairs of the nitrogen and the carbanion being generated. These factors were studied theoretically by various investigators from the standpoint of the theory of hetarynes[171] and α-effects[168, 172].

The above effects should apparently be taken into account also in the study of the characteristics of the chemical behaviour of α,α'-disubstituted pyridines, but as yet there is no information in the literature about this subject.

3. Comparative Reactivities of α,α'- and γ-Substituents in the Pyridine Molecule

The differences between the reactivities of α- and γ-substituents in the pyridine ring, on the one hand, and β-substituents, on the other, have been studied in fair detail[11]. At the same time the comparative reactivities of α-, α'-, and γ-substituents in pyridine compounds have been little investigated. There are as yet no theoretical generalisations in this field and the problem is still mainly in the stage of the accumulation of experimental data. Unfortunately in the series of pyridines, including α,α'-disubstituted and α,α',γ-trisubstituted derivatives, a detailed analysis of the effect of specific solvation and of the influence of various solvents on the reaction mechanism, of the kind carried out, for example, for pyrimidine derivatives[173], has not been performed.

It has been established experimentally that, on heating with an aqueous solution of sodium hydroxide, 2,6-dibromopyridine is fairly smoothly converted into 2,6-dihydroxypyridine, while heating with 70% sulphuric acid even at 160 °C leads only to 6-bromo-2-hydroxypyridine[11]:

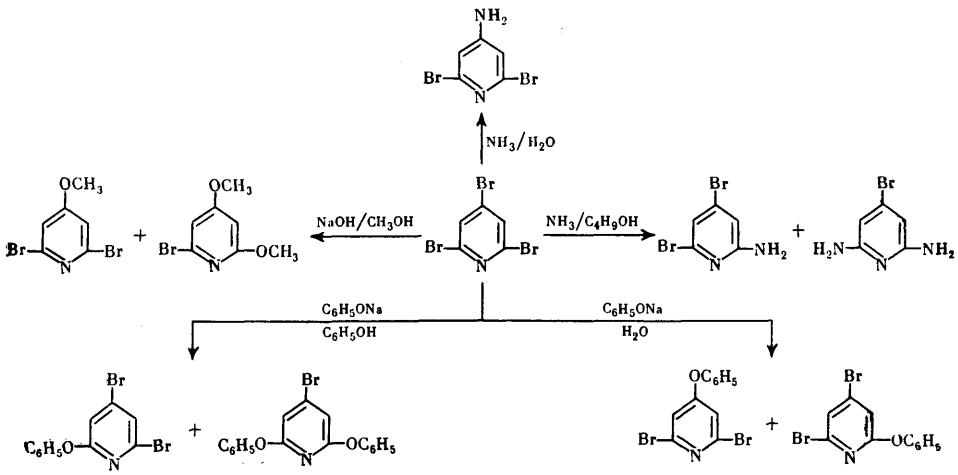


Nucleophilic substitution of 2,4,6-tribromopyridine takes place in the 4- and 2,4-positions in a methanol solution of sodium hydroxide, in the 2- and 2,6-positions in the presence of sodium phenoxide with an excess of phenol, in the 2- and 4-positions in an aqueous solution of sodium phenoxide, in the 4-position in an aqueous solution of ammonia, and in the 2- and 6-positions in a butanol solution of ammonia[11] (see scheme at the top of page 574).

Analogous effects are observed also in the reactions of polyhalogenopyridines. For example, pentachloropyridine reacts with magnesium and butyl-lithium in ether in the 4-position[174]; in methylcyclohexane the same reaction with butyl-lithium takes place only in the 2-position[175-177].

The interaction of pentachloro-,[74] pentabromo-,[178] and pentafluoropyridines[179] with a series of nucleophiles proceeds selectively at the $C_{(4)}$ atom. On the other hand, pentachloropyridine reacts with certain amines only at the $C_{(2)}$ atom[180], while in others it gives rise to a mixture of products of substitution at the $C_{(2)}$ and $C_{(4)}$ atoms[181]. It has been shown recently[182] that the reaction of pentafluoropyridine with pentafluorophenol in the presence of potassium fluoride and 18-crown-6-ether proceeds selectively with substitution of fluorine in the 2-position, although normally this mode of reaction is atypical for pentafluoropyridines[183-185].

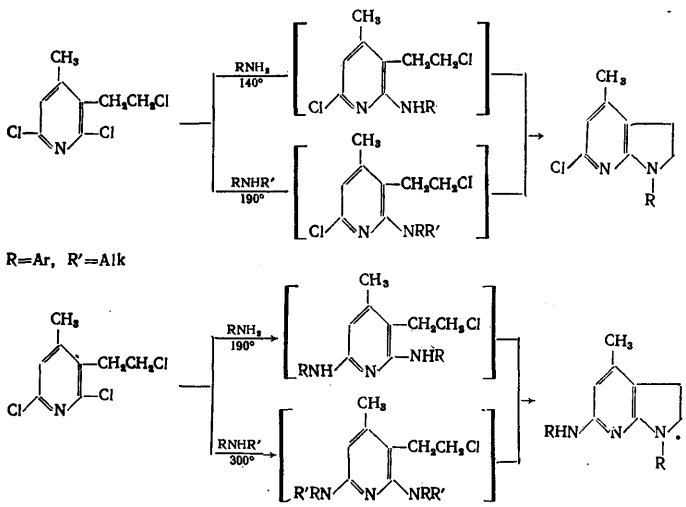
The *N*-sodio-derivative of α-aminopyridine formed in the Chichibabin reaction as a result of the interaction of pyridine with sodium amide is again aminated with sodium amide at a



higher temperature to give 2,6-diaminopyridine. The same compound is also formed on interaction of 2-dimethylaminopyridine with sodium amide; the dimethylamino-group is split off in the form of an *N*-sodio-derivative[186].

In contrast to aromatic diamines, forming 1 : 2 complexes with Lewis acids, 2,6-diaminopyridine combines with only one BF_3 molecule (like 2,4,6-triaminotriazine) to form a 1 : 1 adduct[187]. The hydrolysis of 2,6-diaminopyridine yields only 6-amino-2-hydroxypyridine[11].

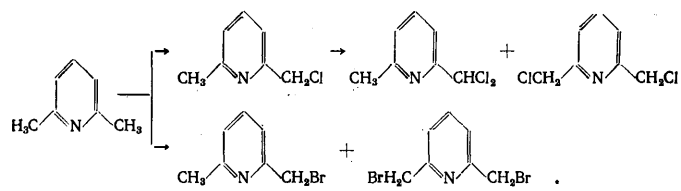
The products of the interaction of substituted 2,6-dichloropyridine (trichlorocollidine) with primary and secondary amines indicate different reactivities of the α- and α'-chlorine atoms in this compound:



The α- and α'-chlorine atoms interact with aromatic amines at 140° and 190 °C respectively[188]; the α-chlorine atom begins to interact with secondary amines of the type of *N*-alkylanilines at 190 °C, while the α'-chlorine atom does not react until 300 °C, *N*-dealkylation occurring in both cases[188-190]. The processes are very sensitive to steric hindrance and the reaction with t-butylamine does not occur at all[188]. After the substitution of the α- or α,α'-chlorine atoms in trichlorocollidine by amine residues, cyclisation involving the β-chloroethyl side chain takes place readily and 7-azaindoline derivatives are formed[189].

Kinetic studies of the oxidation of 2,6-lutidine with potassium permanganate in an aqueous medium showed that the process takes place stepwise and the products corresponding to all oxidation stages are formed even in the earliest stages: 2,6-lutidine → 6-methylpicolinic acid → dipicolinic acid → oxalates → carbonates[142].

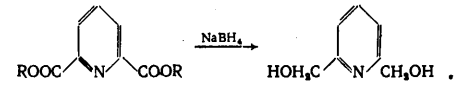
On bromination of 2,6-lutidine with *N*-bromosuccinimide, the monobromo-derivative and the symmetrical dibromo-derivative were isolated in low yields[137]. Further halogenation in CCl_4 at 60 °C in the presence of added sodium carbonate and water of 2-chloromethyl-6-methylpyridine, obtained by the chlorination of 2,6-lutidine, leads to the formation of the asymmetric dichloro-product at a rate which is 3.7 times faster than the formation of the symmetrical product[191]. The opposite results have been described for the reactions of 2,6-lutidine with organolithium compounds[192]:



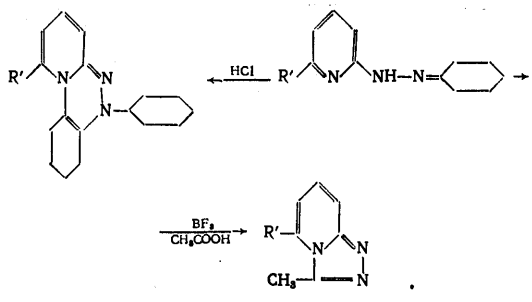
Analysis of the differences between the reactivities of the α,α'- and γ-substituents in the pyridine ring has shown that in many cases the differences are caused by the formation of intermediates with participation of the α,α'-substituents and the pyridine nitrogen atom. For example, it has been established[193] that, in the reduction of isomeric bisalkoxycarbonylpyridines with di-isobutylaluminium hydride, the ester residues in the α,α'-positions of the pyridine ring are the first to be converted into aldehyde groups. This is apparently caused by the favourable energetic factors in the formation of intermediate cyclic products with participation of the complex hydride, the ester groups, and the pyridine nitrogen.

The formation of an intramolecular complex also explains the tendency of pyridine-2,6-dicarboxylate (dipicolinate) esters to be reduced by sodium tetrahydroborate, used in the large-scale industrial synthesis of the medicinal preparation paramidin[135]. Sodium tetrahydroborate does not usually interact with ester groups but dipicolinate esters are reduced by this reagent to 2,6-di(hydroxymethyl)pyridine

in high yields:



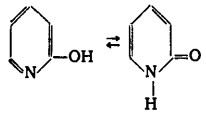
Processes in which the cyclic substances formed are the final reaction products also belong to the class of reactions involving the formation of new rings with participation of the α,α′-substituents and the pyridine nitrogen atom. For example, when 6-bromo- and particularly 6-methyl-2-pyridinylhydrazones of cyclohexanone are treated with hydrochloric acid or the etherate of boron trifluoride in acetic acid, cyclisation via the pyridine nitrogen atom takes place under the conditions of the Fischer reaction. This results in the formation of derivatives of 1*H*-benzo[1,2-*e*]pyrido[2,1-*c*]-*asymm*-triazine and triazolo[4,3-*c*]pyridine:[194–196]



4. Problems of the Tautomerism and the Dual Reactivity of α,α′-Disubstituted Pyridines

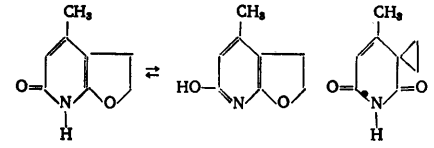
The characteristics of the distribution of electron density in α,α′-disubstituted pyridines, the nature of the protonation and solvation of these compounds have a significant influence on the lactam–lactim tautomerism of 6-substituted 2-hydroxypyridines.

It is known[197–199] that the lactam–lactim tautomeric equilibrium involving α- and γ-hydroxypyridines in aqueous solutions is greatly displaced towards lactams. The enthalpy characterising the extent to which the oxo-form is favoured by energy factors amounts to 14.2 kJ mol^{-1} for α-pyridone[200], while the tautomeric equilibrium constant is 3.0.[197]

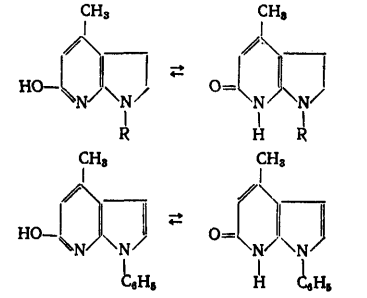


The formation of associated species via intermolecular hydrogen bonds[201–204] and solvation effects[205,206] apparently play an important role. The decrease of the concentration of the test substance in non-polar solvents and an increase of temperature displace somewhat the tautomeric equilibrium in the direction of lactims even in more concentrated solutions [201,207]. For example, at an α-pyridone concentration in cyclohexane of 1.25×10^{-7} M, pK_T decreases to 1.6.[201] However, in this case too the oxo-tautomer predominates[201,208]. It has been established recently by ultraviolet[209] and infrared[213–217] spectroscopy and mass spectrometry[210–212] that only in the gas phase is the tautomeric equilibrium involving α-pyridone displaced towards the hydroxy-form with an equilibrium constant of ~0.4.[201,207,218]

Up to 1966 very little was known about the influence of substituents in α-pyridones in the 6-position on the prototropic lactam–lactim tautomeric equilibrium. Only a report about the differences between the ultraviolet spectra of perchloro-2-pyridone and its *N*-methyl derivative, indicating different chromophoric systems in these compounds, was published[219]. Furthermore, there has been a report, which aroused a wide controversy, concerning the preparative separation of the oxo- and hydroxy-tautomers of 6-hydroxy-4-methyl-2,3-dihydrofuro[2,3-*c*]pyridine, which have different solubilities in ethyl acetate, different melting points, different ultraviolect spectra, and different colour reactions with iron(III) chloride[220]. However, further investigations [221–223] disproved the possibility of isolating individual stable hydroxy- and oxo-tautomers and showed that the second compound is an isomeric product with a spiro-structure:



It was discovered in 1966 [224] that, on passing from α-pyridone to the analogous derivatives of dihydropyrrolo-[2,3-*c*]pyridine (6-hydroxy-7-azaindolines), there is an appreciable shift of the lactam–lactim equilibrium towards lactims. Comparable amounts of both tautomeric forms have been detected in solutions of these compounds by ultraviolet and infrared spectroscopy, but, as a result of a change in the solvent polarity, the equilibrium can be displaced reversibly towards the oxo- or hydroxy-tautomer until it predominates:



On passing from 7-azaindolines to 7-azaindoles, the equilibrium is displaced still more towards the hydroxy-form[225]. For example, infrared spectroscopy failed to detect the lactam form of 6-hydroxy-4-methyl-1-phenyl-7-azaindole either in the crystalline form or in dioxan solution and a weak absorption due to the lactam carbonyl begins to be manifested at 1642 cm^{-1} only in the spectrum of a solution in a more polar solvent—carbon tetrachloride—together with the intense band due to the hydroxy-group of the lactim at 3580 cm^{-1}. Concordant results have been obtained also by ultraviolet spectroscopy using as a reference "fixed" *N*- and *O*-methyl derivatives[225]. The prototropic tautomeric equilibrium is displaced towards the lactim even more in the case of the oxygen analogues of 7-azaindolines—derivatives of 7-azabenzofuran[226].

A change in the junction between the rings, namely the transition from 6-hydroxy-7-aza-compounds to 6-hydroxy-5-azaindoles or benzofurans, causes a sharp weakening of the influence of the heteroatom of the five-membered ring on the position of the tautomeric equilibrium: the predominance of the oxo-form characteristic of α-pyridones is restored for the compounds in the crystalline state and in solutions of different polarity[226]. This permitted the conclusion that a

decisive factor in the effect of the heteroatom of the five-membered ring is its inductive influence, which rapidly decays with distance.

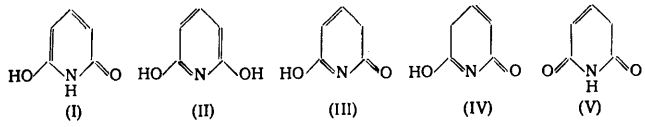
The study of the lactam–lactim equilibria involving monocyclic 6-substituted α-pyridones showed that the tautomeric equilibria of 6-amino- and 6-chloro-2-hydroxy-pyridines are also significantly displaced towards the lactims[227]. Quantitative analysis demonstrated[227] that the effect of the 6-amino-group is somewhat greater if the latter is incorporated in the five-membered ring condensed to pyridine and the influence of hetero-substituents increases, in conformity with their $-I$ effect, in the sequence Cl > OR > NR_2. When the 6-amino-group is acylated, its $-I$ effect diminishes and the tautomeric equilibrium is greatly displaced towards the lactam[228].

Thermodynamic studies have shown[200,229] that the conversion of the lactam into the lactim is an exothermic process for the majority of the solvents investigated. With decrease of solvent polarity, the process becomes less exothermic and in dioxan, where the lactim formed greatly predominates, the process already becomes endothermic. An increase of temperature favours a decrease of the content of the lactam forms in more polar solvents, while in solvents of low polarity the opposite behaviour is observed.

The existence in solutions of comparable amounts of the hydroxy- and oxo-tautomers of 6-chloro-2-hydroxypyridine has been demonstrated, their ratio being proportional to the solvent polarity[72,227,230,231]. The addition of an anionic surfactant (sodium lauryl sulphate) to an aqueous solution of 6-chloro-2-hydroxypyridine has little effect on the tautomeric equilibrium, while the addition of a cationic detergent (cetyltrimethylammonium bromide) shifts the equilibrium towards the lactim form[232].

The predominance of the lactim form has also been described for 5,6-dichloro-2-hydroxy-3,4-diphenylpyridine[233]. Problems concerning the protonation of 6-amino-2-hydroxy-pyridines have been examined in detail[234].

Of the five theoretically possible tautomeric forms (I)–(V) of 2,6-dihydroxypyridine,



(I) (II) (III) (IV) (V)

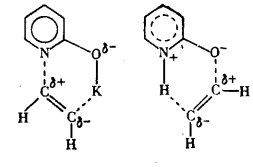
apparently three forms exist in aqueous solutions: (I), (II), and (V) in proportions of 60 : 25 : 15.[222,235–237] The oxolactim (I) predominates not only in water, alcohols, and dimethyl sulphoxide but also in cyclohexane with 5% of added alcohol. The tautomeric equilibrium is displaced towards the lactim to an even greater extent for 2-hydroxy-6-methoxypyridine[238]. The lactam–lactim tautomerism involving comparable amounts of the tautomeric forms has been described also for 2,3,6-dihydroxypyridines[239].

The 5,6-annelation of γ-pyridone via condensation with the dihydrofuran ring leads to a shift in the tautomeric equilibrium towards the lactim, which is greater than for the monocyclic 6-substituted α-pyridones; on the other hand, following condensation with the six-membered tetrahydropyran ring, the shift of the tautomeric equilibrium towards the lactim is smaller than for the monocyclic 6-substituted α-pyridones[240–242].

The displacement of the tautomeric equilibria of α,α′-disubstituted pyridines to the region where there are comparable amounts of the lactam and lactim tautomeric forms made it possible to investigate the more refined influence of the β- and γ-substituents in the pyridine ring on this process[238]. Usually, after the almost complete displacement of the tautomeric equilibria of α-pyridones towards lactams, such influences of the β- and γ-substituents cannot be detected[197,231,243,244]. It has been found that γ-substituents affect mainly the conjugation effect. For example, whereas the introduction of the hydroxy-group in the 6-position of the α-pyridone system displaces the tautomeric equilibrium towards the lactim owing to its $-I$ effect, the same group in the 4-position of the pyridine ring causes some displacement of the equilibrium towards the lactam by virtue of its $+M$ effect, i.e. it exerts the directly opposite effect[238,245]. Electron-accepting substituents in the β-position of the pyridine molecule shifts the tautomeric equilibrium towards the lactam in the absence of additional effects due to intramolecular hydrogen bonds, etc.[238]

It is noteworthy that the mode of the *N*- or *O*-alkylation processes involving 6-substituted 2-hydroxypyridines is not correlated with the position of the lactam–lactim tautomeric equilibrium[224–226]. α-Pyridone is alkylated at the nitrogen atom by dimethyl sulphate in an aqueous alkaline medium. The alkylation of 6-hydroxy-7-azaindolines under the conditions where the tautomeric equilibrium is displaced towards the lactim leads to high yields of the corresponding *O*-methyl derivatives. However, treatment of 6-hydroxy-7-azabenzofurans, whose tautomeric equilibrium is displaced towards the lactim to an even greater extent, with dimethyl sulphate in an aqueous alkaline medium again gives rise to high yields of *N*-methyl derivatives[227]. A similar behaviour has been observed also in the reactions with diazomethane. α-Pyridone forms virtually only the *O*-methyl derivative, 6-amino-2-hydroxypyridine gives rise to a mixture of equal amounts of the *O*- and *N*-methylated products, while 6-chloro-2-hydroxypyridine, whose tautomeric equilibrium is displaced towards the lactim to an even greater extent, is methylated predominantly at the nitrogen atom[227].

Evidently dynamic reaction factors and not the position of the tautomeric equilibrium play a decisive role in the alkylation of α-hydroxy-derivatives of *N*-heteroaromatic compounds. The view, which remained current for a long time, that the ratio of the amounts of methylation products can indicate the position of the tautomeric equilibrium in the initial compound is therefore erroneous. This claim is also supported by the formation of different proportions of *N*- and *O*-vinyl derivatives when α-pyridones react with acetylene, as a function of the catalyst employed—from 66 : 1 (in the presence of potassium hydroxide) to 23 : 75 (in the presence of cadmium acetate). Shostakovskii et al.[246] assumed that this is associated with the existence of two types of intermediate cyclic vinylation products.



Quantitative determination of the positions of alkylotropic equilibria of the type of 2-methoxypyridine–1-methyl-2-pyridone from the heats and the equilibrium constants showed that in all cases the lactam forms predominate, the enthalpy differences amounting to 50.6 ± 3.3 and 32.2 ± 9.6 kJ mol^{-1} for the liquid and gas phases respectively[247,248]. The introduction of the methyl group in the 6-position of the pyridine ring has little effect on the equilibrium position. On passing to the 6-chloro-derivative, the enthalpy difference decreases significantly owing to the electron-accepting effect of the chlorine atom: to 17.2 ± 9.2 kJ mol^{-1} for the liquid phase and to 1.3 – 15.5 kJ mol^{-1} for the gas phase.

Calculation of the aromaticity of 2-methoxypyridine and 1-methyl-2-pyridone showed that it amounts to ~20% of that of benzene[249], which is consistent with the values of the aromaticity of α-pyridone calculated previously[217,250]. Unfortunately quantum-chemical calculations based on the geometrical optimisation of the α-pyridone system did not yield results in agreement with experiment[251,252].

Thus studies on the chemistry of α,α'-disubstituted pyridines revealed in recent years new features which are of general theoretical interest. At the same time these investigations have also posed new problems associated with the mechanism of the transmission of the effects of α,α'-substituents in heteroaromatic systems, the nature of the mutual influence of the α- and α'-functional groups, etc. The solution of these problems has an importance going quite far beyond the framework of the individual types of pyridine derivatives.

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Antioxidant Stabilisation of Polymers

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Physicochemical aspects of the stabilisation of polymers are discussed. Attention is paid mainly to the aging and stabilisation of polymers under processing conditions. Topics considered are the kinetics and mechanism of the high-temperature oxidation of polymers, critical phenomena in the inhibited oxidation of polymers, the theory of synergism and antagonism among antioxidants, the reasons for differences in efficiency of antioxidants, and certain aspects of the relation between the efficiency of antioxidants and their molecular structure. A list of 132 references is included.

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I. INTRODUCTION

Physical and chemical processes, combined under the general term *aging*, begin immediately after formation of a polymer or a polymeric material. Oxygen and other components of the environment—ozone, water, etc.—are involved. Aging is accelerated by rise in temperature by light, by strong ionising radiations, and by mechanical stresses, being especially rapid under processing conditions for thermoplastic polymers.

We shall disregard the aging of polymers by light, one of the chief reasons for their deterioration under operating conditions, and also those types of aging that are specific to solid polymers. We shall concentrate on chemical processes occurring in polymer melts at high temperatures in the absence and in the presence of oxygen, frequently termed thermal and thermo-oxidative degradation†.

II. THERMO-OXIDATIVE DEGRADATION OF POLYMERS

If the polymer is processed in air, or if it has been stored in air before processing and contains dissolved oxygen, it will undergo thermo-oxidative degradation during processing. This type of polymer degradation has been studied the most thoroughly.

Many references have been made[1,2] to the great similarity in mechanism between the oxidation of polymers and the liquid-phase oxidation of hydrocarbons. On the other hand, little attention has been paid until recently to the differences between the oxidation of substances of low and of high molecular weight. Liquid-phase oxidation of the former is usually investigated at relatively low temperatures, not exceeding 130–150 °C, owing to their high partial vapour pressures at the experimental temperature, whereas the processing temperature of a polymer may exceed 200 °C. No information has appeared on the liquid-phase oxidation of lower hydrocarbons at such high temperatures.

† The term *degradation* frequently denotes only those processes that are accompanied by a decrease in molecular weight or degree of polymerisation.

We shall first consider those stages of oxidation that are common to compounds of low and high molecular weight. Oxidation of a hydrocarbon RH is regarded as a complicated radical chain reaction with degenerate chain branching involving the main states outlined below[3,4].

(*a*) Chain generation has been represented as either a uni-, bi-, or ter-molecular reaction:

$$RH \xrightarrow{k_0} R^{\cdot} + H^{\cdot} \qquad (1)$$

$$RH + O_2 \xrightarrow{k_0'} R^{\cdot} + HO_2^{\cdot} \qquad (2)$$

$$2RH + O_2 \xrightarrow{k_0''} 2R^{\cdot} + H_2O_2 . \qquad (3)$$

(*b*) Chain propagation (growth) occurs as follows:

$$R^{\cdot} + O_2 \xrightarrow{k_1} RO_2^{\cdot} \qquad (4)$$

$$RO_2^{\cdot} + RH \xrightarrow{k_2} ROOH + R^{\cdot} . \qquad (5)$$

(*c*) Chain branching results from unimolecular breakdown of a hydroperoxide, reaction of a hydroperoxide with the hydrocarbon (polymer), or interaction of two hydroperoxy-groups:

$$ROOH \xrightarrow{k_4} RO^{\cdot} + {}^{\cdot}OH \qquad (6)$$

$$ROOH + RH \xrightarrow{k_4'} RO^{\cdot} + R^{\cdot} + H_2O \qquad (7)$$

$$2ROOH \xrightarrow{k_4''} RO_2^{\cdot} + RO^{\cdot} + H_2O . \qquad (8)$$

The radicals RO$^{\cdot}$ and HO$^{\cdot}$ are assumed to react rapidly with the surrounding material to form alkyl radicals R$^{\cdot}$:

$$RO^{\cdot}({}^{\cdot}OH) + RH \rightarrow ROH(H_2O) + R^{\cdot} . \qquad (9)$$

Breakdown of the radical RO$^{\cdot}$ may yield alkyl radicals of lower molecular weight: for example[5]

$$C_6H_5-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-O^{\cdot} \rightarrow C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3 + {}^{\cdot}CH_3 . \qquad (9a)$$

(*d*) Chain termination results from the recombination or disproportionation of any two free radicals involved in the

oxidation:

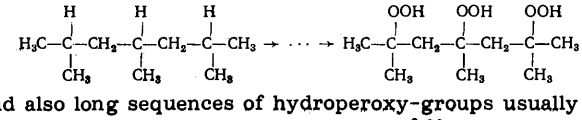
$$2R^{\cdot} \xrightarrow{k_0} R_2 \qquad (10)$$

$$R^{\cdot} + RO_2^{\cdot} \xrightarrow{k_0'} ROOR \qquad (11)$$

$$2RO_2^{\cdot} \xrightarrow{k_0''} ROOR + O_2 . \qquad (12)$$

Considering the individual stages in greater detail, we note that chain generation has hitherto been the last studied. It probably occurs by reaction (2), but in real polymers chains may be generated also by reactions of various impurities[6], in particular metals of variable valency (primarily iron), peroxides, and other compounds.

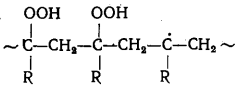
As to the chain-propagating reactions (4) and (5), the majority of authors hold completely identical views. In compounds of fairly high molecular weight and in polymers, however, reaction (5) can take place in two ways: the radical $RO_2^{\cdot}$ can detach a hydrogen atom either from a neighbouring molecule or from an adjacent carbon atom in its own molecule. The latter path gives di- and even tri-hydroperoxides in yields comparable with that of the monohydroperoxide[7,8]



(13)

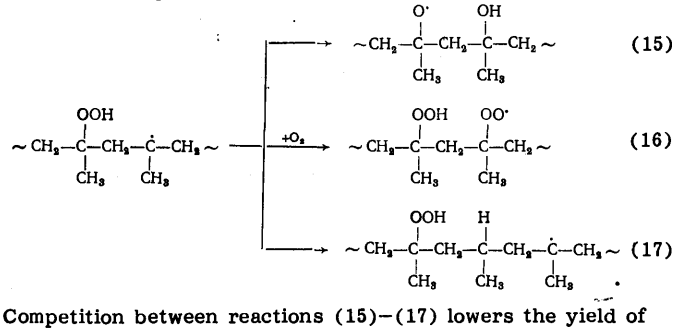
and also long sequences of hydroperoxy-groups usually occupying β positions in polyolefin molecules[9,10].

Propagation of the kinetic oxidation chain involves the formation of peroxyalkyl radicals



(14)

within an individual macromolecule. In such radicals an unstable hydroperoxy-group is always located near the free valency. Interaction of this valency with a hydroperoxy-group that has just been formed leads to loss of the latter. Other possible conversion paths for the peroxyalkyl radical—addition of an oxygen molecule and detachment of a hydrogen atom from the next monomer unit—result in removal of the reaction centre away from the hydroperoxy-group and stabilisation of the group[11]:



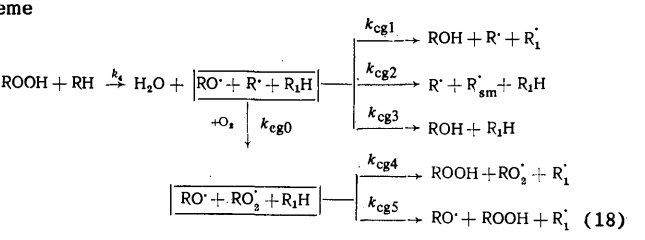
(15) (16) (17)

Competition between reactions (15)–(17) lowers the yield of hydroperoxide in the oxidation of polymers below that observed with analogues of low molecular weight, and the yield becomes dependent on the oxygen pressure. Whereas the oxidation of lower compounds gives hydroperoxide yields close to 100%,[4] only 5–40% is obtained in the oxidation of polyolefins[11–15].

Breakdown of a hydroperoxy-group into RO$^{\cdot}$ and HO$^{\cdot}$ radicals requires the consumption of large quantities of energy (~170 kJ mole^{-1} [16]) and apparently occurs only in the gas phase. In the liquid phase and especially in the molten polymer reactions (7) and (8) are more probable[9,17].

Considering reaction (7) for definiteness, we note that interaction of a hydroperoxy-group in a polymer with a monomer unit in the same or a neighbouring macromolecule produces a pair of free valencies (usually in the form of the radicals R$^{\cdot}$ and RO$^{\cdot}$) located either on neighbouring macromolecules or on a small segment of the same molecule. In a polymer the low translational mobility of a macromolecule is combined with the relatively high vibrational mobility of its segments necessary for the recombination of radicals. For this reason the major proportion of the radicals formed from a hydroperoxide will disappear immediately after formation. In order that breakdown of the hydroperoxy-group should lead to formation of two new kinetic chains (such secondary chain generation as a result of chemical transformation of reaction products is termed *degenerate chain branching*) the free valencies should move sufficiently far apart—should escape from the "cage" formed by molecules of the surrounding material.

In a polymer direct diffusion of primary radicals plays no appreciable part in the escape of radicals from the cage. Three other possibilities remain: one of the radicals of a pair may interact with a neighbouring monomer unit in the same or another macromolecule R_1H, it may react with an oxygen molecule, or the radical RO$^{\cdot}$ may break down with formation of a mobile small radical $R_{sm}^{\cdot}$. The main stages in the breakdown of a hydroperoxide can be represented by the scheme



(18)

in which a cage containing a pair of radicals together with segments of macromolecules R_1H is enclosed in a frame. Each reaction of one of the radicals increases the distance between the free valencies, and the probability of recombination diminishes rapidly. Neglecting for simplicity the probability of recombination of the secondary radicals $R_1^{\cdot}$ and $R_{sm}^{\cdot}$, we find for the mean yield of free radicals formed on the breakdown of ROOH the formula

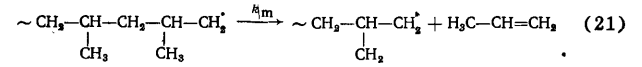
$$\delta = \frac{w_r}{k_4[\mathrm{ROOH}]\,[\mathrm{RH}]} = \frac{2\,(k_{cg0}[O_2] + k_{cg1} + k_{cg2})}{k_{cg0}[O_2] + k_{cg1} + k_{cg2} + k_{cg3}}, \qquad (19)$$

This expression can be expanded as a series of powers of $[O_2]$. If the oxygen concentration is not too high ($[O_2] \ll k_3/k_{cg0}$) only two terms need be retained, so that[18]

$$\delta = \delta_0 + \delta_1[O_2]. \qquad (20)$$

Existence of such a relation at oxygen pressures over the polymer up to 1 atm has been established experimentally[18–20]. One of the experimental proofs will be examined below.

Radicals R$^{\cdot}$ in a polymer may be either terminal or central depending on whether the free valency is located at or remote from the end of a macromolecule. Radicals with a free valency at the end of the chain $R_e^{\cdot}$ are able to eliminate a monomer:



(21)

Reaction (21) involves no change in the number of terminal radicals, and therefore is disregarded in their balance. Radicals $R_e^{\cdot}$ are consumed mainly by reaction with oxygen (4), and the resulting radicals ReOO$^{\cdot}$ detach hydrogen from the

next monomer unit to form not terminal but central radicals $R_c^{\cdot}$.

From the balance equation for R_e

$$d[R_e^{\cdot}]/dt = \delta k_4 [ROOH][RH] - k_1 [R_e^{\cdot}][O_2], \quad (22)$$

we find, putting $\delta = \delta_e + \delta_1[O_2]$, that the dependence on the oxygen pressure of the rate of depolymerisation accompanying decomposition of a polymer hydroperoxide is

$$w_m = \frac{k_4 k_m}{k_1}[RH][ROOH]\{\delta_1 + \delta_0/[O_2]\}. \quad (23)$$

If $\delta_1 = 0$, i.e. if the yield of free radicals on decomposition of the polymer hydroperoxide is independent of the oxygen pressure, it follows from (23) that the rate of formation of monomer will tend to zero with rise in oxygen pressure; if $\delta_1 > 0$, however, it will tend to a limit other than zero.

The initial rate of formation of propene has been measured[20] in the decomposition of two types of polypropylene hydroperoxide: the usual hydroperoxide was obtained by oxidising polypropylene with molecular oxygen at 130 °C, and a postirradation sample was formed by heating to room temperature a specimen of the polymer first saturated with oxygen and exposed to a small dose of γ-rays. The postirradiation hydroperoxide contained isolated hydroperoxy-groups surrounded by unoxidised material. Fig.1 shows that the rate of formation of propene from both hydroperoxides tended to a finite limit or remained constant: i.e. in both cases the yield of free radicals increased under the influence of oxygen.

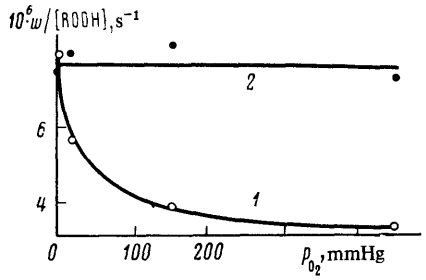


Figure 1. Dependence[20] on oxygen pressure at 130 °C of rate of formation of propene by the decomposition of polypropylene hydroperoxide prepared by: *1*) oxidation of polypropylene at 130 °C; *2*) postirradiation oxidation at room temperature.

Because of the competition between reactions (15)–(17) the sequence of hydroperoxy-groups includes unoxidised units and other functional groups, e.g. hydroxy, the proportions of which depend on the conditions of oxidation. During decomposition some of the hydroperoxy-groups break down, and new functional groups will appear on the polymer chain, not necessarily identical with those formed in the primary reactions. All this makes the concept of "polymer hydroperoxide" extraordinarily indefinite, and is the reason for the disagreement in published values of constants for "the same" hydroperoxide.

Termination of the oxidation chain can occur on the interaction of any two free radicals involved in the reaction. Not only macroradicals can take part in chain termination but also "light" radicals[21] formed by the breakdown of RO$^{\cdot}$ radicals, as in reaction (9a). The recombination of two macroradicals may lead to their cross-linking, which is accompanied by increase in the molecular weight of the linear polymer and even by formation in it of three-dimensional structures, often termed the "gel fraction" as a consequence of insolubility in substances that dissolve the unoxidised polymer[22].

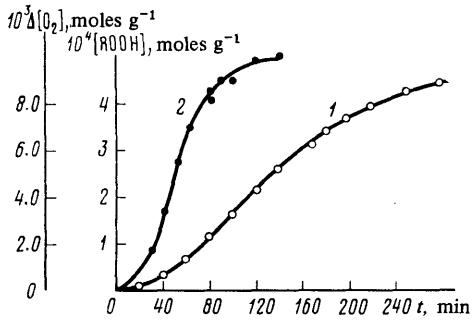


Figure 2. Oxidation of solid isotactic polypropylene[18] under an oxygen pressure of 400 mmHg at 130 °C: *1*) absorption of oxygen; *2*) accumulation of hydroperoxides.

The oxidation of polymers at not very high temperatures is autocatalytic[15–17]. This is explained by the increase rate of formation of free radicals with increase in hydroperoxide concentration, but the time of autocatalysis is of the same order of magnitude as the lifetime of the hydroperoxide, i.e. the reciprocal of its decomposition rate constant. Fig.2 shows a typical curve for the absorption of oxygen during the oxidation of a polymer (polypropylene). The curve has the sigmoid form characteristic of autocatalytic processes. Fig.2 shows that the times for attaining maximum rate of absorption of oxygen and maximum concentration of hydroperoxide are approximately the same.

The initial rate of absorption of oxygen in the oxidation is often too small to be measured, and only after some time, termed the *induction period*, does it increase sufficiently to begin to affect instruments used to observe the reaction. The dependence on the oxygen pressure p of the induction period τ in the oxidation of polymers is described in several cases by the formula[23,24]

$$\tau = a + bp^{-1}, \quad (24)$$

in which a and b are constants depending in particular on the sensitivity of the instrument recording the absorption of oxygen. The coefficients a and b vary with temperature according to the Arrhenius law, with effective activation energies calculated from their variation that are negative and usually differ from each other.

III. HIGH-TEMPERATURE OXIDATION OF POLYMERS

Long induction periods—from tens of minutes to several years—are usually observed in the oxidation of polymers (in the absence of stabilisers) at their working temperatures. With rise in temperature the induction period rapidly becomes shorter, and in the vicinity of 200 °C is already measured in

tens of seconds. At higher temperatures any induction period in oxidation becomes completely imperceptible.

The mechanism of the oxidation of polymers changes at 280–300 °C. The main stage of the chain propagation reaction (5) is replaced by breakdown of the peroxy-radical:

$$RO_2^{\cdot} \xrightarrow{k_{7a}} {}^{\cdot}OH + \text{Inactive products} \qquad RO_2^{\cdot} \xrightarrow{k_{7b}} R_1^{\cdot} + \text{Inactive products} \quad . \tag{25}$$

Such a reaction was first suggested by Enikolopyan[25] to explain the negative temperature coefficient of oxidation in the gas phase; he estimated its activation energy as ~85 kJ mole^{-1}. The isomerisation of $RO_2^{\cdot}$ radicals in polyethylene has been assumed[25] to involve the reactions

$$\sim CH(O{-}O^{\cdot})-CH_2\sim \rightarrow \sim CH(O)-CH\sim + {}^{\cdot}OH \tag{26}$$

$$\sim CH(O{-}O^{\cdot})-CH_2\sim \rightarrow \sim C(=O)-CH_2\sim + {}^{\cdot}OH \quad . \tag{27}$$

The occurrence of (26) is indicated by the formation of α-oxide groups in polyethylene that has been oxidised at temperatures above 300 °C. The carbonyl groups formed by several mechanisms are observed in polyethylene oxidised at any temperature; their content is greatest when oxidation has occurred at 300 °C. We can also complete the scheme by the reactions of HO$^{\cdot}$ radicals—chain transfer

$$RH + {}^{\cdot}OH \xrightarrow{k_8} R^{\cdot} + H_2O \tag{28}$$

and chain termination

$$R^{\cdot} + {}^{\cdot}OH \xrightarrow{k_9} ROH \quad . \tag{29}$$

If we write a set of balanced equations for the radicals R$^{\cdot}$, $RO_2^{\cdot}$, and HO$^{\cdot}$ and the hydroperoxide, and solve them by Bodenstein's method[27] on the assumption that the kinetic chains are long, i.e. that the rate of reaction (28) exceeds substantially that of (29), we obtain for the rate of high-temperature oxidation of a polymer containing aliphatic groups (RH) the formula[26]

$$w = \delta k_1 k_2 k_8 [RH]^2 [O_2]/2k_{7a}k_9. \tag{30}$$

According to (30) the rate of oxidation of a polymer, which varies little with oxygen pressure at low temperatures, becomes proportional to the concentration and hence pressure of oxygen at high temperatures. This conclusion is extremely important, since it shows that a polymer might be protected from oxidation by brief heating (e.g. during processing), by restricting the access of oxygen, or by introducing into the polymer absorbents for oxygen[28]. The last method can be used only for the short-term protection of a polymer from oxidation at high temperatures, being unsuitable for its protection under conditions of prolonged storage or operation in air. This question will be discussed in greater detail below.

In Fig.3 rate curves for the absorption of oxygen during the oxidation of polyethylene at 360 °C [? see Fig.3] under various oxygen pressures are plotted as $\lg(p_0/p)$ against time. The initial segments of these curves are straight lines. We shall show that this indicates proportionality between rate and oxygen pressure.

In a closed volume V the change in the quantity of oxygen N_{O_2} (in moles per kilogram of polymer) is related to the change in its pressure $-\Delta p$ by the formula

$$N_{O_2} = V(-\Delta p)/RTm, \tag{31}$$

in which m is the mass of the oxidisable specimen. If the rate of absorption of oxygen during the reaction is proportional to its concentration in the polymer $dN_{O_2}/dt = k_{exp}[O_2]$, while the concentration of oxygen in the polymer depends on its pressure above the polymer in conformity with Henry's law $[O_2] = \gamma p$, we can write

$$\frac{d}{dt}\left\{\frac{V(-\Delta p)}{RTm}\right\} = k_{exp}\gamma p. \tag{32}$$

Transferring p to the left-hand side, and dt to the right-hand side, and integrating the resulting equation from 0 to t and from p_0 to p, we finally obtain

$$\ln(p_0/p) = RTm\gamma k_{exp}t/V \quad . \tag{33}$$

Thus if the reaction velocity is proportional to the oxygen concentration, the kinetic curve becomes a straight line in the above coordinates, the slope of which is independent of the oxygen pressure, as is observed experimentally (Fig.3).

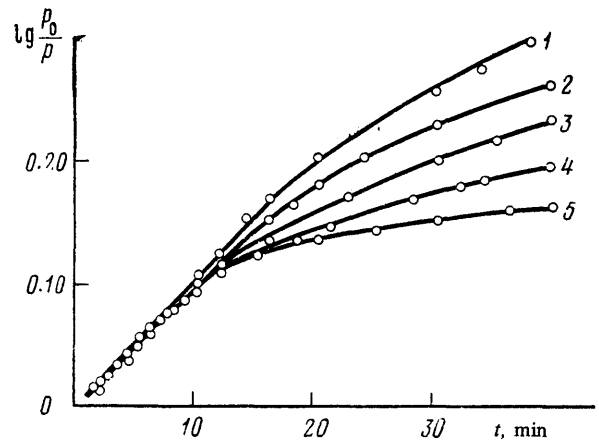


Figure 3. Absorption of oxygen in the high-temperature oxidation of polyethylene (melt)[26] at 300 °C [? see text] under different pressures (mmHg): *1*) 20; *2*) 40; *3*) 60; *4*) 80; *5*) 100.

The demoninator of formula (30) contains the quantity k_{7a}, whose temperature variation corresponds to an activation energy of ~85 kJ mole^{-1}. Rapid increase in the denominator with temperature should slow down the increase in rate (under otherwise similar conditions). Indeed, the rate of oxidation of polyethylene increases slightly with temperature above 300 °C, at which δ in the numerator of (30) reaches its stoichiometric limit ($0 \leq \delta_{max} \leq 2$). In the temperature range intermediate between low- and high-temperature oxidation a more complicated pattern is observed: the rate of absorption of oxygen diminishes with rise in temperature at low pressures (up to 60 mmHg), but at higher pressures it increases. The dependence on the oxygen pressure of the maximum rate of absorption of oxygen in the oxidation of high-density polyethylene is shown in Fig.4.

The monomer units of many thermostable polymers contain small aliphatic groups, mostly methylene or dimethylmethylene together with large aromatic or heterocyclic groups. When oxygen acts on such polymers, these aliphatic groups are the first to be oxidised. The rate is described by formula (30):

i.e. it is proportional to the oxygen pressure, and its temperature variation corresponds to low activation energies, in the range 20–80 kJ mole^{-1}. In some cases the rate of oxidation, decreasing as the aliphatic fragments are consumed, remains proportional to the square of the concentration of remaining methylene groups, as also follows from formula (30).

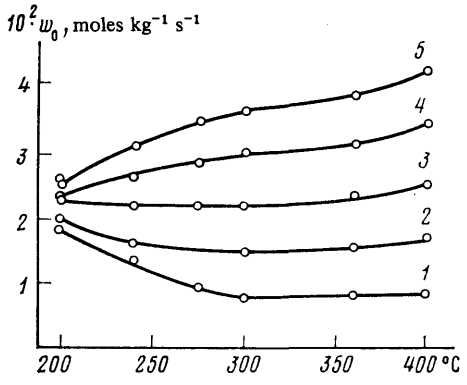


Figure 4. Temperature dependence of maximum rate of absorption of oxygen in the oxidation of polyethylene[26] under different oxygen pressures: *1*)–*5*) as in Fig. 3.

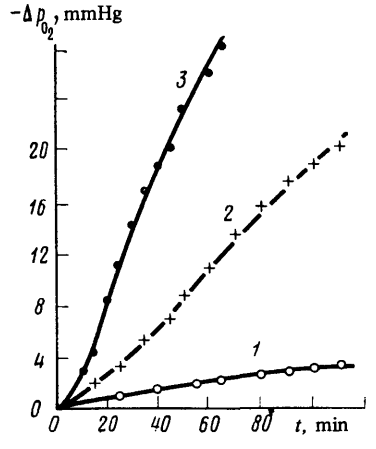


Figure 5. Absorption of oxygen during the oxidation of a polysulphone containing isopropylidene groups ~C(CH$_3$)$_2$~ in the chain[29] under an oxygen pressure of 150 mmHg at different temperatures (°C): *1*) 300; *2*) 350; *3*) 400.

The oxidation of aliphatic groups in a macromolecule may initiate oxidative degradation of aromatic groups, which in the absence of methylene groups takes place at temperatures up to 350–400 °C with considerably smaller velocities[29]. A sharp decrease in rate is observed[30] after the exhaustion of methylene groups, and it was suggested that high-temperature oxidation converted the latter mainly into ketone groups, without degradation of the macromolecules (polybenzoxazole[30]).

Oxidation of a polymer (a polysulphone containing phenylene and isopropylidene groups) at temperatures up to 400 °C was observed[29] to follow an autocatalytic course lasting tens of minutes (Fig. 5). Such long times of autocatalysis cannot be attributed to accumulation of hydroperoxides, since the lifetimes of the latter at such high temperatures are measured in fractions of a second, whereas the period of autocatalytic progress has the same order of magnitude as the lifetime of the product Pr responsible for autocatalysis. In order to show the existence of such a relation we examine the balance equation for this product.

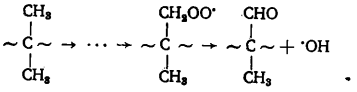
$$d[Pr]/dt = \varkappa w_{O_2} - k_{Pr}[Pr], \qquad (34)$$

in which w_{O_2} is the rate of absorption of oxygen and $\varkappa$ the yield of the product per mole of oxygen absorbed. Assuming to a first approximation that the rate w_{O_2} is constant, we find that

$$[Pr] = \frac{\varkappa w_{O_2}}{k_{Pr}}(1 - e^{-k_{Pr}t}). \qquad (35)$$

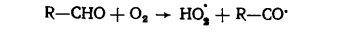
According to this formula the concentration of the product will differ from its maximum value of $\varkappa w_{O_2} k_{Pr}^{-1}$, by 10% when $\exp(-k_{Pr}t) = 0.1$ or at $t = 2.3\, k_{Pr}^{-1}$ and by 1% at $t = 4.6 k_{Pr}^{-1}$, whereas the lifetime of the product is k_{Pr}^{-1}.[27]

Autocatalysis in the high-temperature oxidation of polymers may be due to the formation of aldehyde groups[29]:

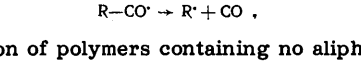


(36)

Oxidation of such groups may provide an additional source of free radicals[31]:

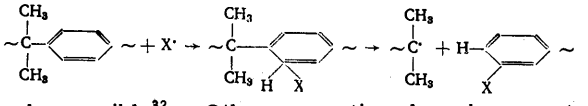


(37)



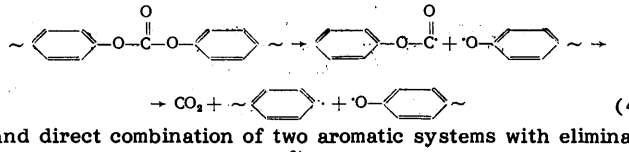
(38)

The oxidation of polymers containing no aliphatic groups is far slower. The mechanism of their interaction with oxygen has not been reliably established. Besides detachment of hydrogen atoms from aromatic systems followed by addition of oxygen to the resulting macroradicals and small radicals reactions of the type



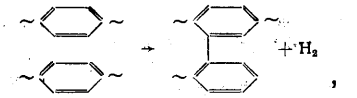
(39)

are also possible[32]. Other suggestions have been rupture of the main chain into two macroradicals[33]



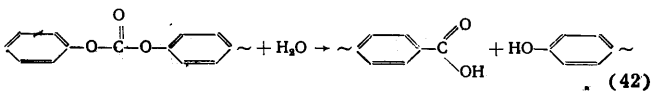
(40)

and direct combination of two aromatic systems with elimination of a hydrogen molecule[34]



(41)

Water formed at various stages in the high-temperature oxidation of heterochain polymers may be involved in reactions leading to rupture of the polymer chain[35]:



(42)

Not only HO· radicals but also other simple radicals—$CH_3^·$, $CH_3OO^·$, $C_6H_5^·$, etc.,—may be involved in the oxidation of polymers at high temperatures. The more reactive radicals take part mainly in chain-transfer reactions, and the less reactive in chain termination.

IV. CHEMICAL REACTIONS UNDERLYING THE STABILISATION OF POLYMERS

The properties of a polymeric material can be stabilised during thermo-oxidative degradation by two fundamentally different methods—by lowering the overall rate of oxidation or by eliminating individual undesirable consequences of the reaction, e.g. discoloration resulting from the accumulation of particular chromophoric groups in the polymer.

As already mentioned, the oxidation of organic compounds by molecular oxygen is a free-radical chain reaction with degenerate chain branching, i.e. with branching caused by reactions of intermediate products formed in the main chain reaction. The overall rate of the chain reaction can be diminished either by increasing the rate of chain termination or by decomposing the intermediate products involved in branching.

In 1947 Bolland and ten Have[36,37] suggested and substantiated a mechanism of chain termination in the oxidation of phenolic antioxidants in which a phenol molecule reacts with a peroxy-radical, donating to the latter a hydrogen atom and forming a hydroperoxide molecule and a relatively inactive free radical incapable of propagating the chain:

$$RO_2^· + ArOH \rightarrow ROOH + ArO^· . \qquad (43)$$

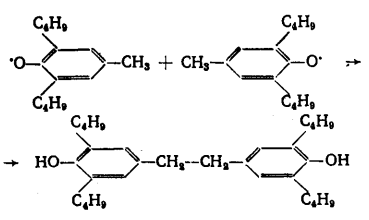
The subsequent fate of the inactive phenoxyl radical has been the subject of many investigations[36-46]. Among conversion products of the antioxidant have been found various compounds formed by dimerisation of phenoxy-radicals and also compounds of quinoid structure, which may result from oxidation and disproportionation of these radicals. Thus the antioxidant quinol is converted into the quinone, probably by interaction of the primary ArO· radical with a second peroxy-radical[37]:



(44)

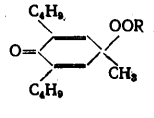
Formation of a quinone may result from disproportionation of two hydroxyphenoxy-radicals[38] or their reaction with an oxygen molecule.

The widely used antioxidant 2,6-di-t-butyl-4-methylphenol (Ionol) is known to yield dimerisation products of the primary radical[39-41]



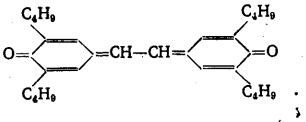
(45)

products of interaction of peroxy- and phenoxy-radicals[39]



(46)

and products of further conversion of compounds formed by dimerisation of ArO· [39,41]



(47)

However, the majority of phenoxy-radicals formed from this inhibitor under the usual conditions (non-sensitised) of the oxidation of polypropylene interacted to form intensely coloured products of high molecular weight. On further oxidation these products disappeared[42]. The radicals can also take part in chain transfer[43,44]:

$$ArO^· + RH \rightarrow ArOH + R^· . \qquad (48)$$

A scheme analogous to (43) was suggested[43,47] for chain termination by aromatic amines:

$$RO_2^· + R_1R_2NH \rightarrow ROOH + R_1R_2N^· . \qquad (49)$$

In 1954 Boozer and Hammond[48,49] proposed a different mechanism of chain termination, in which the antioxidant molecule initially adds a peroxy-radical reversibly to form a complex, which reacts with a second peroxy-radical to give an inactive product:

$$RO_2^· + A \rightleftharpoons ARO_2^· \qquad (50)$$

$$ARO_2^· + RO_2^· \rightarrow \text{Products} . \qquad (51)$$

This suggested mechanism has been criticised by many workers[46,50,51]. It was shown that "ordinary" oxidation inhibitors—phenols and aromatic amines—terminate oxidation chains in conformity with Eqn.(43) or (49). However, certain relatively ineffective antioxidants, such as anthracene and carbon black, were later shown to retard the oxidation of polyalkenes by the Boozer–Hammond mechanism of chain termination[48], i.e. by catalysing quadratic (involving the interaction of two active centres) termination of the oxidation chain[52,53].

It is interesting that phenols and amines, which react rapidly with peroxy-radicals, hardly interact if at all with alkyl radicals R·. Thus Dolgoplosk et al.[54] showed that, in the absence of oxygen, phenols and secondary aromatic amines do not retard the polymerisation of styrene and several other monomers, and only slightly retard that of allyl and vinyl acetates; in the presence of oxygen the same phenols and amines effectively inhibit the polymerisation of all these monomers. Similar observations were reported by other workers[55]. Vasil'ev showed[56] that, in the absence of oxygen, the antioxidant 2,6-di-t-butylphenol remains unconsumed in ethylbenzene containing an initiator.

According to Eqns.(43) and (49) interaction of a phenol or an amine molecule with a peroxy-radical gives a hydroperoxide molecule or a hydroperoxy-group, capable of breaking down subsequently into two free radicals. It was suggested[57] that relatively inactive free radicals could be used as antioxidants in order to eliminate this side-effect. In practice, however, such radicals proved to be relatively inactive antioxidants, since the concentration of alkyl radicals in the compound undergoing oxidation was extremely low in comparison with that of peroxy-radicals, while the "inactive" nitroxyl radicals at the high concentrations necessary for stabilisation played an appreciable part in the initiation of oxidation[58]. In those cases in which such radicals nevertheless retarded oxidation effectively it was found[59] that

they were first reduced to the corresponding aromatic amines:

$$2Ar_2NO^{\cdot} + x\,RH \rightarrow Ar_2NH + \text{Products} \ . \qquad (52)$$

In this process one amine molecule formed from two "stable" radicals; furthermore, it is accompanied by degradation of the polymer, so that it is more advantageous to introduce into the latter not the radical $Ar_2NO^{\cdot}$ but the corresponding aromatic amine.

Quinones behave similarly to "stable" radicals. Thus benzoquinone when heated in a hydrocarbon is slowly converted into a mixture of quinol and its mono- and di-ethers, which are actual inhibitors[60]. The view was also expressed[61] that quinones retard oxidation by reacting with $R^{\cdot}$ radicals.

Aromatic phosphites are also capable of terminating oxidation chains. The mechanism is apparently extremely complicated: these compounds can be hydrolysed to phenols, and can reduce peroxides and interact directly with peroxy-radicals. It was suggested[62,63] that this last reaction is represented by the equation

$$RO_2^{\cdot} + (ArO)_3P \rightarrow RO(ArO)_2PO + ArO^{\cdot} \ . \qquad (53)$$

Organic sulphides and phosphites (phosphorous esters) slow down oxidation by a mechanism involving decomposition of intermediate products. The first reports[64,65] of increase in the rate of decomposition of hydroperoxides in the presence of organic sulphides showed that purely aliphatic sulphides react most rapidly with hydroperoxides, mixed sulphides react more slowly, and aromatic sulphides hardly react at all. The antioxidant properties of these sulphides in the oxidation of white oil vary in the same sequence. Both during oxidation and on interaction with hydroperoxides the sulphides first pass into sulphoxides and then into sulphones:

$$ROOH + R_1{-}S{-}R_1 \rightarrow ROH + R_1{-}\overset{\overset{O}{\|}}{S}{-}R_1 \qquad (54)$$

$$ROOH + R_1{-}\overset{\overset{O}{\|}}{S}{-}R_1 \rightarrow ROH + R_1{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}R_1 \ . \qquad (55)$$

These observations have been confirmed many times by other workers[66,67]. The yield of free radicals in reactions between hydroperoxides and sulphides is extraordinarily low, not exceeding one radical per thousand hydroperoxide molecules that have reacted[68].

Organic phosphites react with hydroperoxides by a similar mechanism[63]:

$$ROOH + P(OR_1)_3 \rightarrow ROH + O{=}P(OR_1)_3 \ . \qquad (56)$$

Several phosphites, e.g. iso-octyl diphenyl phosphite, are considerably more efficient than organic sulphides in reducing hydroperoxides[69].

V. KINETICS OF THE INHIBITED OXIDATION OF POLYMERS

Reductants of hydroperoxides are seldom used as individual antioxidants for polymer materials[70], but are usually employed mixed with substances that terminate oxidation chains, i.e. oxidation inhibitors in the narrow sense. The latter, however, are used both as individual antioxidants and as the main components of mixed antioxidants. Both cases will be discussed below.

As mentioned above, the chief substances used as oxidation inhibitors are phenols and secondary aromatic amines, of general formula IH. Because of their great reactivity such inhibitors, when introduced into a polymer undergoing oxidation, take part in all stages of the oxidation chain—generation, propagation, branching, and termination—and react with all types of free radicals formed in the polymer. The primary products formed from the inhibitors may undergo further reactions. All this makes the mechanism of inhibited oxidation extremely complicated. Below we shall take the mechanism of inhibited oxidation to mean the minimum set of main stages necessary for a quantitative description of the observed regularities.

The main stage at which oxidation is inhibited is chain termination

$$RO_2^{\cdot} + IH \rightarrow ROOH + I^{\cdot} \ . \qquad (57)$$

The resulting $I^{\cdot}$ radicals may be involved in chain transfer by interacting with the oxidisable material:

$$I^{\cdot} + RH \rightarrow IH + R^{\cdot} \ . \qquad (58)$$

If reaction (58) were the sole means of consumption of the relatively inactive radicals $I^{\cdot}$, they would sooner or later accumulate in sufficient concentration for the rate of reaction (58) to become comparable with that of (57). For every chain terminated there would then be a chain initiated by an $I^{\cdot}$ radical: i.e. the inhibitor would cease to influence the reaction velocity.

The situation is unaffected by taking into account the reaction of $I^{\cdot}$ radicals with alkyl radicals $R^{\cdot}$, for the concentration of the latter in the polymer is negligible in comparison with that of $RO_2^{\cdot}$. Because of the great viscosity of the medium and the near immobility of the macroradicals $R^{\cdot}$ and $RO_2^{\cdot}$ the rates of their reactions with IH molecules and $I^{\cdot}$ radicals will be determined by the frequency with which the reactant species meet, so that the difference in the reactivity of different substances towards the polymer radicals becomes insignificant. For example, the rate constants of the reactions of macroradicals with inhibitor molecules and inactive radicals in polystyrene differ by the factors of at most 10–15.[71]

Let us suppose for definiteness that the rate constant of reaction (57) amounts to 10% of that of the process

$$I^{\cdot} + R^{\cdot} \rightarrow RI \qquad (59)$$

while the concentration of $R^{\cdot}$ radicals is 1% of that of $RO_2^{\cdot}$ radicals. Then the rate of consumption of inhibitor radicals $I^{\cdot}$ will become equal to the rate of their formation only when $[I^{\cdot}]/[IH] = 10$, i.e. after almost all the inhibitor has been converted into radicals. Thus reaction (59) cannot effectively remove $I^{\cdot}$ radicals from the polymer.

With the same relative rate constants and radical concentrations the reaction

$$I^{\cdot} + RO_2^{\cdot} \rightarrow ROOI \qquad (60)$$

will occur at the same rate as the formation of $I^{\cdot}$ provided that $[I^{\cdot}]/[IH] \geq 0.1$. In a medium of low molecular weight reaction (60) converts an inactive $I^{\cdot}$ radical and an active $RO_2^{\cdot}$ radical into the quinolide peroxide(46),[39,72] but in a polymer it produces a peroxy-group "grafted" to the polymer chain. Breakdown of such a peroxy-group will yield two new radicals, apparently more active than their precursors. At the fairly high temperatures at which polymers are processed the peroxy-groups will break down almost instantaneously: i.e. reaction (60) may lead to conversion of an inactive $I^{\cdot}$ radical into an active $RO^{\cdot}$ radical.

Thus for a given substance effectively to inhibit the oxidation of a polymer it is necessary not only that the chain-termination (57) rate constant should be sufficiently high but also that termination should yield an inactive radical $I^{\cdot}$ that should be sufficiently rapidly consumed in reactions not

involving the polymer, e.g. recombination—such as (45)—or disproportionation

$$2I^{\cdot} \xrightarrow{k_6} \text{Products}, \qquad (61)$$

In fact the concentrations of inhibitor radicals formed in the oxidation of polypropylene with initial inhibitor concentrations of $(7-9)\times10^{-2}$ mole kg^{-1} do not exceed 10^{16} $g^{-1} = 1.7\times10^{-5}$ mole kg^{-1}: i.e. they are <1% of the inhibitor concentration[73]. Thus such reactions do indeed play an important part in the consumption of inhibitor radicals. The concentration of the latter (measured accurate to an unknown factor) has been shown[74] to be proportional to the square root of the rate of consumption of the inhibitor:

$$[I^{\cdot}] = \text{const}\left(-\frac{d[IH]}{dt}\right)^{1/2}, \qquad (62)$$

This is consistent with a mechanism of consumption of $I^{\cdot}$ radicals by recombination or disproportionation, when

$$d[I^{\cdot}]/dt = -d[IH]/dt - k_6[I^{\cdot}]^2. \qquad (63)$$

With $d[I^{\cdot}]/dt = 0$ when a steady concentration of the radicals is reached, we obtain for $[I^{\cdot}]$ an expression of the form (62).

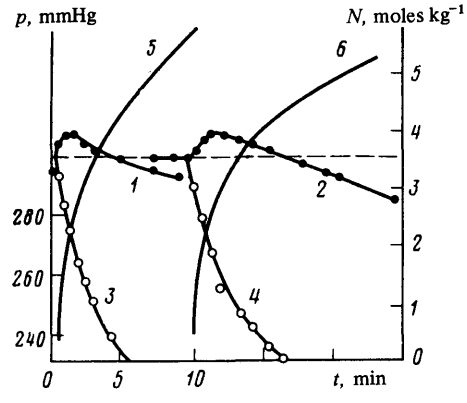


Figure 6. Effect of the inhibitor methylene-2,2′-bis-(4-methyl-6-t-butylphenol)—Antioxidant 22–46 (0.1 mole kg^{-1})—on the oxidation of polyethylene[75] under an initial pressure of 300 mmHg (broken line) at 260 °C: *1*) variation in total pressure in absence of inhibitor; *2*) as (1) in presence of inhibitor; *3*) partial oxygen pressure without inhibitor; *4*) partial oxygen pressure with inhibitor; *5*) formation of volatile products (*N*) without inhibitor; *6*) as (5) with inhibitor.

Fig. 6 illustrates the absorption of oxygen during the oxidation of polypropylene at 260 °C in the absence and in the presence of an inhibitor, the variation in total presssure in the reaction vessel, and the quantity of volatile degradation products evolved from the polymer during oxidation. It is evident that the inhibitor—in this case methylene-2,2′-bis-(4-methyl-6-t-butylphenol), known also as *Antioxidant 22–46*—merely delayed for some time the start of a rapid process characterised by a high rate of absorption of oxygen together with a high rate of formation of volatile degradation products[75]. The induction period from the start of the reaction to the rapid stage is short in the absence of an inhibitor, being measured at high temperatures in fractions of a second, but is lengthened by an inhibitor, sometimes by factors of 10^2–10^4. When oxidation passes into the rapid stage, the molecular weight and consequent properties of the polymer change rapidly, "disastrously", the material becomes unsuitable for practical use, and articles made from it disintegrate. Henceforward, therefore, we shall be interested only in processes occurring during the induction period.

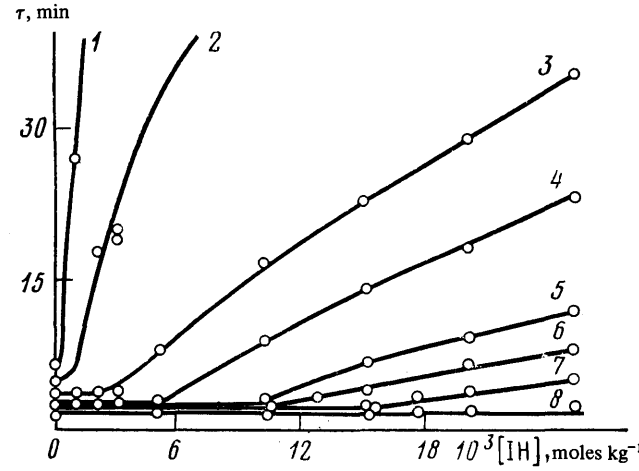


Figure 7. Dependence of induction period in the oxidation of polyethylene on concentration of Antioxidant 22–46 under 300 mmHg [76] at different temperatures (°C): *1*) 200; *2*) 220; *3*) 230; *4*) 240; *5*) 250; *6*) 260; *7*) 265; *8*) 270.

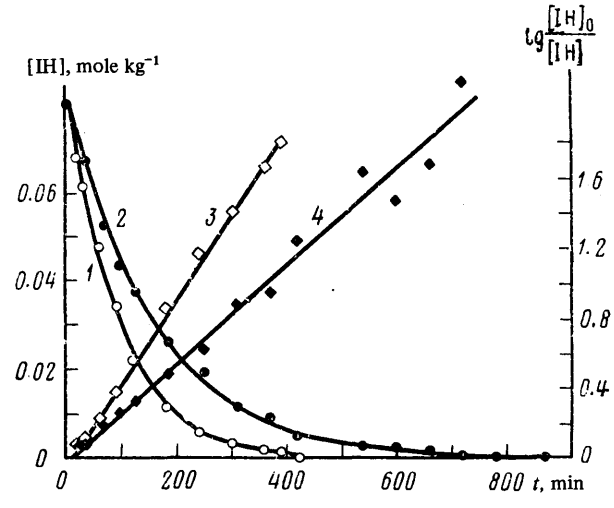


Figure 8. Effect of didecyl sulphide (0.08 mole kg^{-1}) on variation in concentration of Antioxidant 22–46 during induction period in the oxidation of polypropylene[80] under an oxygen pressure of 300 mmHg at 200 °C: *1*) sulphide absent; *2*) sulphide present; *3*) as (*1*) plotted for a first-order reaction; *4*) as (*3*) in the presence of sulphide.

Fig.7 illustrates the dependence of induction period on inhibitor concentration at various temperatures. Up to a certain critical concentration the inhibitor has hardly any effect, but beyond it the induction period increases with concentration. The critical concentration increases rapidly with temperature, while the slope of the curves diminishes. Around 280–290 °C, i.e. at temperatures at which the mechanism of oxidation changes, the "usual" antioxidants cease to retard oxidation, and their critical concentrations increase to several tenths of a mole per kilogram, i.e. 3–10 mass % and even above. Use of such high antioxidant concentrations is obviously inadmissible for the most diverse reasons, beginning with cost and ending with their marked effect on the properties of the polymer material.

The polymer does not remain unchanged during the induction period. Firstly the antioxidant (inhibitor) it contains is consumed. The corresponding curve can be linearised by plotting $\lg([IH]/[IH]_0]$ against time (Fig.8). Kinetic curves for a first-order reaction, described by formulae such as

$$-d[IH]/dt = k[IH], \quad (64)$$

$$[IH] = [IH]_0 e^{-kt} \quad (65)$$

become straight lines in such coordinates[27].

Increasing the vertical scale in Fig.8 would reveal that the slow consumption of inhibitor, which up to a certain time obeys a first-order law, accelerates sharply at the end of the induction period. This is immediately followed by a marked increase in the rate of absorption of oxygen: i.e. the induction period is complete. Consumption of the inhibitor accelerates immediately its concentration falls below this critical concentration. Denoting by τ_{cr} the portion of the induction period from attainment of the critical concentration to the start of the rapid reaction, assuming that the inhibitor concentration falls from $[IH]_0$ to $[IH]_{cr}$ during the time interval $\tau - \tau_{cr}$, substituting these values in Eqn.(65), and taking logarithms, we obtain the formula

$$\tau = \tau_{cr} + \frac{1}{k} \ln \frac{[IH]_0}{[IH]_{cr}} \quad (66)$$

relating the induction period with the concentration of inhibitor in the initial polymer[77,78]. This provides a good description of the experimental dependence of the induction period in the oxidation of polymers on the initial inhibitor concentration in all cases in which conversion products of the inhibitor have little effect on the rate of oxidation. A logarithmic dependence of induction period on inhibitor concentration was established empirically by Rosenwald[79], who studied the oxidation of petrol.

Fig.8 shows that, if a substance that reduces hydroperoxy-groups [didecyl sulphide $(C_{10}H_{21})_2S$] is introduced into a polymer containing an oxidation inhibitor, the first-order consumption of inhibitor is maintained, but the absolute value of the rate constant is lower[80].

During the induction period the molecular weight of the polymer decreases. At sufficiently high inhibitor concentrations—several times the critical value—an approximately linear relation exists between the rate of degradation of polymer chains and the inhibitor concentration, which breaks down only when the latter has fallen to roughly double the critical concentration, after which the rate of degradation increases sharply[81] (Fig.9). With few exceptions[69] reductants of hydroperoxy-groups do not lower the rate of polymer degradation. The rate of absorption of oxygen shows a similar dependence on the inhibitor concentration[82].

Volatile products, in particular monomers[74,83], are formed during the induction period in the inhibited oxidation of polyethylene and polypropylene, but their rates of formation are low ($\sim 10^{-9}$ mole kg^{-1} s^{-1} at 200 °C), and at sufficiently high inhibitor concentrations are independent both of such concentrations[74,83] and of the oxygen pressure[74].

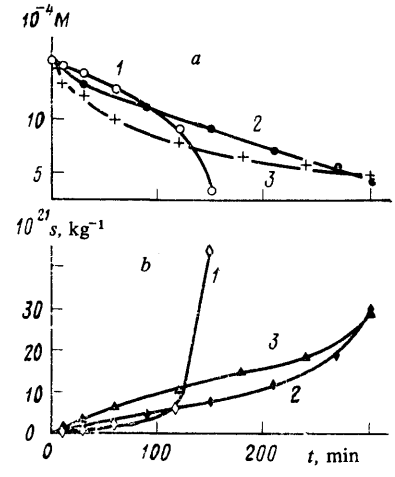


Figure 9. Variation in (*a*) molecular weight and (*b*) number of breaks in polymer chain during induction period in the inhibited oxidation of polypropylene under 300 mmHg at 200 °C in the presence of Antioxidant 22-46 at different initial concentrations (mole kg^{-1}): *1*) 0.004; *2*) 0.025; *3*) 0.0625.

Thus, as had been pointed out in the early work on inhibited oxidation[84], antioxidants do not arrest polymer oxidation and the accompanying degradative processes but merely lower their rates considerably.

According to the original theory an inhibitor terminates the kinetic oxidation chain and is itself thereby consumed[85] at a rate

$$-d[IH]/dt = \frac{1}{j} w_n, \quad (67)$$

where w_n is the rate of chain generation and j the stoichiometric inhibition coefficient, i.e. the number of free radicals destroyed by one inhibitor molecule. Comparison of Eqns. (66) and (67) clearly reveals agreement between experiment and theory if $w_n = k[IH]$, i.e. if the rate of chain generation is proportional to the inhibitor concentration, which can be explained only by involvement of the inhibitor in chain generation[86,87].

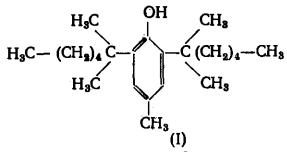
The aromatic amines and alkylated phenols used as inhibitors are considerably more reactive than the polymers they protect, not only towards peroxy-radicals but also towards molecular oxygen. For this reason, even at low (subcritical) inhibitor concentrations, the reaction

$$IH + O_2 \xrightarrow{k_8} I^{\cdot} + HO_2^{\cdot} \xrightarrow{(RH)} \cdots \rightarrow R^{\cdot} \quad (68)$$

occurs at rates exceeding the rate of chain generation in the absence of an inhibitor, i.e. reactions (1)–(3),[77,78,80]

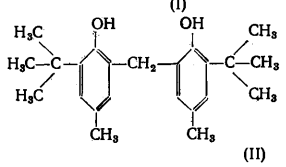
One reason for the difference in antioxidant efficiency between inhibitors belonging to the same class of compounds may be a difference in the rate constants of reaction (68). However, even compounds that are very similar in chemical

nature may differ very greatly in antioxidant efficiency. Thus the alkylphenols (I) and (II)



(69)

(I)



(70)

(II)

at equal concentrations of the phenolic hydroxyls give induction periods in the oxidation of polypropylene differing by factors of ten in length[77]. It might have been supposed that this was due to a difference in reactivity between the hydroxyls in (I) and (II), but experiment showed that the difference was qualitative in character: the introduction of variable concentrations of (I) into a polymer containing a constant concentration of (II) produced a greater shortening of the induction period the higher the concentration of (I), although such introduction of a second inhibitor increased the total inhibitor concentration (Fig. 10). When a reductant for hydroperoxide (didecyl sulphide) was introduced into the polymer together with the inhibitors, the qualitative difference between (I) and (II) disappeared: just as in the case illustrated in Fig. 7, the sulphide produced inflexions in the concentration dependence of the induction period, above which the length of the latter increased rapidly (Fig. 11),[80] and the consumption of the inhibitor followed a first-order curve (Fig. 12).

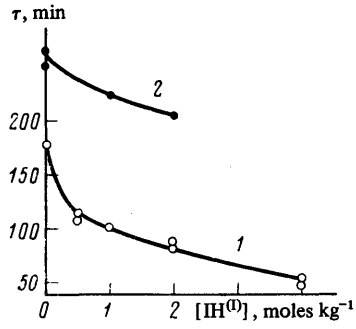
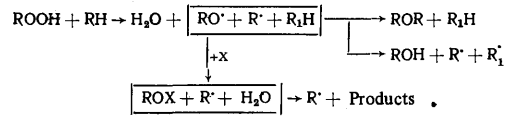


Figure 10. Dependence of induction period in the oxidation of polypropylene[77] under 300 mmHg of oxygen at 200 °C on concentration of inhibitor (I) for different contents of (II) (mole kg^{-1}): *1*) 0.01; *2*) 0.02.

In view of such behaviour of inhibitor (I) the difference could not be explained even on the assumption of a considerably greater rate of direct oxidation (68) of (I) than of (II). It was suggested that the difference between the monohydric (I) and dihydric (II) phenols was due to this difference in the number of active functional groups involved in chain termination[77,80,88].

In a substance undergoing oxidation free radicals appear and disappear in pairs. The pair formed on breakdown of a hydroperoxy-group most probably recombine, so that the yield of free radicals in this reaction is small (scheme 18). A hypothetical species X that might have destroyed only one of the radicals would have made recombination impossible for the other radical:



(71)

If in the absence of X the yield of radicals from the cage exceeds unity, the introduction of X will lower the yield of free radicals formed by decomposition of the hydroperoxy-group (and of any source of radicals in general). If, however, this yield is less than unity, X will increase the yield of free radicals.

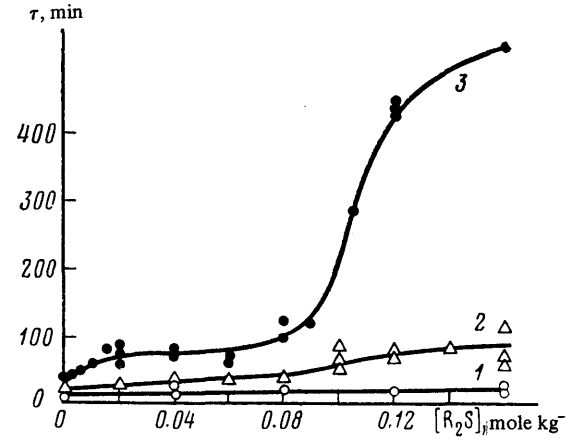


Figure 11. Dependence of induction period in the oxidation of polypropylene[80] under 300 mmHg of oxygen at 200 °C on the concentation of inhibitor (I) in the presence of different contents (mole kg^{-1}) or didecyl sulphide (R_2S): *1*) 0; *2*) 0.04; *3*) 0.08.

In order to estimate the possible effect we assume that recombination in a cage is so rapid that it can involve those X molecules that were present on formation of the cage. If the volume of the cage is taken to be $(10\ \text{Å})^3 = 10^{-24}$ litre, one litre of the polymer will contain 10^{24} cages. On introduction into the polymer of X at a concentration 0.01 M = 6×10^{21} $litre^{-1}$ only 0.6% of the cages will contain X and, if in all these cages the yield of radicals changes from the original value δ_0 to unity, the observed yield of radicals in the presence of X will be $\delta_0 + 0.006(1-\delta_0)$, which will differ appreciably from the original value δ_0 only if the latter does not exceed 0.01.

Real inhibitors will obviously differ from the above substance X. Reaction between an inhibitor and an active radical forms a relatively inactive radical I$^\cdot$ capable of recombination with the other radical of the pair; but the lower activity of I$^\cdot$ than of RO$^\cdot$ or R$^\cdot$, and also the increase in

mean distance between the radicals after each step in the reaction, will lead to a change in the yield of radicals from the cage if an inhibitor molecule enters it. Increase in the number of active functional groups in the inhibitor molecule will obviously increase the probability that the molecule will interact simultaneously with the two radicals of the pair: i.e. a phenolic diol should not increase the yield of radicals from the cage, or should increase it far less than would a monophenol.

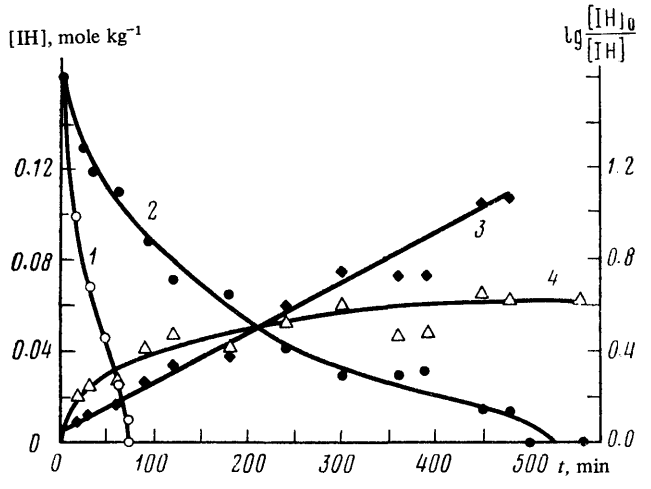


Figure 12. Consumption of inhibitor (I) during induction period in the oxidation of polypropylene[60] under 300 mmHg of oxygen at 200 °C: *1*) in absence of sulphide; *2*) in presence of didecyl sulphide (0.08 mole kg^{-1}); *3*) as (*2*) plotted as lg ($[IH]_0/[IH]$) against time; *4*) inhibitor vaporised from specimen containing sulphide.

Pudov[89,90] observed that inhibitors increased the yield of free radicals formed by the breakdown of hydroperoxy-groups in polypropylene. He showed that in the absence of an inhibitor the yield per hydroperoxy-group decomposed was ~10^{-2} radical, and the appreciable effect of the introduction of inhibitors into the polymer is consistent with the above estimates. In contrast, the yield of free radicals on the decomposition of lower peroxides or azo-compounds is 0.2–1.0, so that attempts to change this yield by means of inhibitors were unsuccessful[91].

Mono- and di-amines differ in effectiveness similarly to mono- and di-phenols: under comparable conditions diamines considerably surpass monoamines in antioxidant efficiency[92].

The presence of two hydroxy-groups in a phenol molecule is a necessary but not sufficient condition for the simultaneous entry of two phenolic hydroxyls into a cage containing a pair of radicals: it is necessary also that these groups should be located side by side in the most probable conformations of the diphenol molecule. Infrared spectra have been used[93] to determine the relative arrangement of hydroxy-groups. The close approach of two such groups leads to formation of a hydrogen bond O–H...O–H, corresponding in dilute solutions of the diphenol to an absorption band at 3440–3460 cm^{-1}. A hydrogen bond between a hydroxy-group and the π-electron system of an adjacent aromatic ring corresponds to a band at 3520–3550 cm^{-1}, and a free hydroxyl gives a band at 3630–3660 cm^{-1}.[94] The experiments show[93] that only those diphenols are effective antioxidants in whose molecules the hydroxy-groups are linked by a hydrogen bond, bond, i.e. are situated close together in the main conformation. The inhibitor 3,3',5,5'-tetra-t-butylbiphenyl-2,2'-diol, which differs from (II) in the absence of a methylene group between rings, has a unique conformation with OH...π hydrogen bonds, in which the hydroxy-groups are far apart, and is therefore an ineffective antioxidant. The effectiveness of (II) is greatly diminished also when one of its hydroxyls is replaced by an ester group[95].

Another possible mechanism by which an inhibitor can affect the yield of free radicals formed from a hydroperoxy-group is direct interaction between this group and the inhibitor molecule[96,97]:

$$ROOH + IH \rightarrow RO^{\cdot} + I^{\cdot} + H_2O \rightarrow \cdots \rightarrow \delta R^{\cdot}. \qquad (72)$$

The dependence of the yield of free radicals on the hydroperoxide concentration can be written (independently of the mechanism) as the series

$$\delta = \delta_0 + \delta_t [IH] + \delta_{tt} [IH]^2 + \ldots \qquad (73)$$

or at low inhibitor concentrations

$$\delta = \delta_0 + \delta_t [IH]. \qquad (74)$$

Thus with sufficiently high inhibitor concentratons, when the stages of chain generation (1)–(3) and quadratic chain termination (10)–(12) can be neglected, oxidation can be represented by the stages[88]

$$\begin{gathered} IH + O_2 \xrightarrow{k_0} I^{\cdot} + HO_2^{\cdot} \xrightarrow{(RH)} \cdots \rightarrow \alpha R^{\cdot} \\ R^{\cdot} + O_2 \xrightarrow{k_1} RO_2^{\cdot} \\ RO_2^{\cdot} + RH \xrightarrow{k_2} ROOH + R^{\cdot} \\ RO_2^{\cdot} + IH \xrightarrow{k_3} ROOH + I^{\cdot} \\ ROOH + RH \xrightarrow{k_4(IH,O_2)} \delta R^{\cdot} + \text{Products} \\ ROOH + R_2S \xrightarrow{k_5} \text{Products} \end{gathered} \qquad (75)$$

which give rise to the balance equations

$$d[R^{\cdot}]/\alpha\, t = d\, k_0 [IH] [O_2] + k_2 [RO_2^{\cdot}] [RH] + \delta k_4 [ROOH] [RH] - k_1 [R^{\cdot}] [O_2], \qquad (76)$$

$$d[RO_2^{\cdot}]/d\, t = k_1 [R^{\cdot}] [O_2] - k_2 [RO_2^{\cdot}] [RH] - k_3 [RO_2^{\cdot}] [IH], \qquad (77)$$

$$[OH]/d\, t = k_2 [RO_2^{\cdot}] [RH] + k_3 [RO_2^{\cdot}] [IH] - k_4 [ROOH] [RH] - k_5 [ROOH] [R_2S] \qquad (78)$$

for $R^{\cdot}$, $RO_2^{\cdot}$, and ROOH.

If the process takes place at a sufficiently high temperature, at which the lifetime of hydroperoxy-groups is short compared with the duration of the reaction, we can attempt to solve Eqns.(76)–(78) by Bodenstein's method[98], i.e. by neglecting rates of change of the instantaneous radical and hydroperoxide concentrations in comparison with their rates of formation and consumption, equating $d[R^{\cdot}]/dt$, $d[RO_2^{\cdot}]/dt$, and d[ROOH]/dt to zero. The set of differential equations (76)–(78) then becomes a set of algebraic equations, which can readily be solved by the usual methods. It then follows from Eqn.(78) that the steady-state concentrations of peroxy-radicals and hydroperoxy-groups are related by the formula

$$[ROOH] = \frac{k_2 [RH] + k_3 [IH]}{k_4 [RH] + k_5 [R_2S]} [RO_2^{\cdot}]. \qquad (79)$$

Substituting for [ROOH] in (76) and solving simultaneously the resulting equation and (77), we find for the steady-state

concentration of peroxy-radicals

$$[RO_2^{\cdot}]_{st} = \alpha k_0 [IH] [O_2] \cdot \left[k_3 [IH] - \frac{\delta k_4 [RH] (k_2 [RH] + k_3 [IH])}{k_4 [RH] + k_5 [R_2S]} \right]^{-1}. \quad (80)$$

This will be finite (i.e. inhibited oxidation of a polymer will be a steady-state process) only if the antioxidant concentration exceeds some critical value

$$[IH]_{cr} = \delta k_2 k_4 [RH]^2 \cdot \{(1-\delta) k_3 k_4 [RH] + k_3 k_5 [R_2S]\}^{-1}, \quad (81)$$

i.e. the critical inhibitor concentration. When $[IH] < [IH]_{cr}$, the rate $d[RO_2^{\cdot}]/dt$ will increase without limit: i.e. Bodenstein's method will be inapplicable[99].

The physical significance of the critical concentration is that below it the oxidation will be autocatalytic (non-stationary) until the rate is limited by quadratic chain termination (12), but above this concentration the process will be stationary and occur at a very low rate. On the curves representing the dependence of the oxidation induction period on inhibitor concentration the critical concentration corresponds to a sharp inflexion, after which the induction period begins to increase with concentration[100] (Fig.6).

Substituting in (81) for δ from (74) and putting $[R_2S] = 0$, we obtain the quadratic equation

$$\delta_i k_3 [IH]^2_{cr} + (\delta_i k_2 [RH] - (1-\delta_0) k_3) [IH]_{cr} + \delta_0 k_2 [RH] = 0 \quad (82)$$

for the critical concentration of an inhibitor that increases the probability of degenerate chain branching. When

$$0 \leqslant \delta_i < (1-\delta_0^{1/3})^2 k_3 / k_2 [RH]$$

the quadratic equation has two positive real roots: i.e. an inhibitor that branches kinetic chains has two critical concentrations, and oxidation is a steady-state process only when the inhibitor concentration lies between them. An inhibitor for which the above relation exists between the constants δ_0, δ_i, k_2, and k_3 is an antioxidant of moderate strength[101].

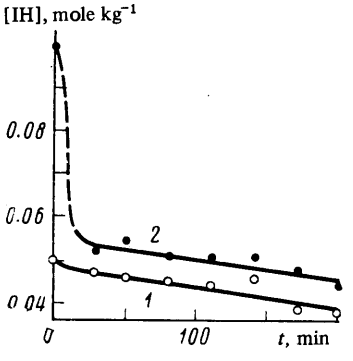


Figure 13. Variation in concentration of phenyl-2-naphthylamine in the initial stage of the induction period in the oxidation of polypropylene[104] under 300 mmHg of oxygen at 200 °C for different initial concentrations (mole kg^{-1}): *1*) 0.05; *2*) 0.10.

The lower (usual) critical concentration has been observed many times in the oxidation of simple compounds[102,103] and polymers[77,78,80,100]. The upper critical concentration appears as a sharp increase in rate of consumption of inhibitor above some concentration (Fig.13), which sometimes (not necessarily) slows down abruptly after the excess of inhibitor above the upper critical concentration has been consumed, or as a sharp "ceiling" (Fig.14) or maximum (Fig.15) in the dependence of induction period on inhibitor concentration. Whereas the rate of degradation of the polymer initially decreases and then smoothly increases with inhibitor concentrations in the range between lower and upper critical values, above the latter this rate increases sharply[104-106].

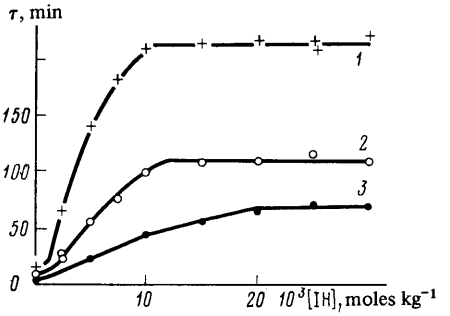


Figure 14. Dependence of induction period in the oxidation of polypropylene[105] under 300 mmHg of oxygen on concentration of methylene-2-2'-bis-(4-chloro-6-t-butylphenol) at different temperatures (°C): *1*) 180; *2*) 190; *3*) 200.

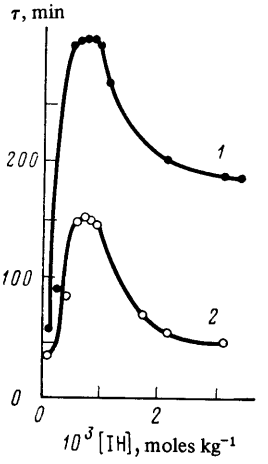


Figure 15. Dependence of induction period in the oxidation of an indene–coumaric resin[106] under 300 mmHg of oxygen on concentration of methylene-2,2'-bis-(4-methyl-6-t-butylphenol) at different temperatures (°C): *1*) 150; *2*) 180.

If in (82) we put $k_3[IH] \ll k_2[RH]$, i.e. confine our attention to low inhibitor concentrations, we find for the lower critical concentration of a moderately strong antioxidant the approximate formula[101]

$$[IH]_{cr} = \delta_0 k_2 [RH] \cdot (k_3 - \delta_i k_2 [RH])^{-1}. \quad (83)$$

The rate of consumption of the inhibitor can be written as the sum of the rates of its direct oxidation by molecular oxygen and its reaction with $RO_2^{\cdot}$ radicals:

$$-\frac{d[IH]}{dt} = k_0[IH][O_2] + \alpha k_0 k_3 [IH]^2 [O_2] \times$$
$$\times \left[k_3[IH] - \frac{\delta k_4 [RH](k_2[RH] + k_3[IH])}{k_4[RH] + k_5[R_2S]}\right]^{-1}. \quad (84)$$

When $[IH] \gg [IH]_{cr}$, the second term in the demoninator is small in comparison with $k_3[IH]$, and Eqn.(84) represents first-order consumption of the inhibitor. An inhibitor in whose presence δ remains approximately constant, and whose first-order rate of consumption is maintained even in the absence of R_2S, has been termed a *strong antioxidant*[80].

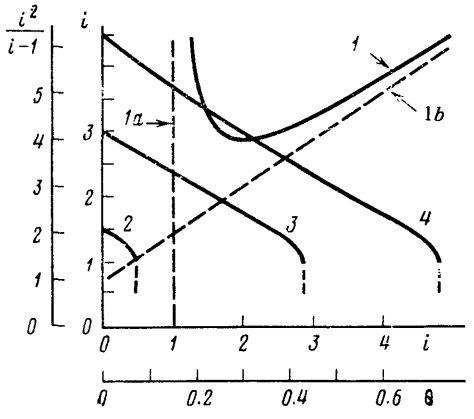


Figure 16. Calculation from Ref.101 of: *1*) dependence of dimensionless rate of consumption of an antioxidant of medium strength $w = i^2/(i-1)$ on its instantaneous concentration i; *1a,b*) asymptotes corresponding to (1); *2*)–*4*) variation in dimensionless concentration of the antioxidant with the dimensionless time θ during the oxidation induction period for different initial concentrations.

The law governing consumption of a moderately strong antioxidant can be found by substituting for δ from (74) in (84). Assuming also that $[R_2S] = 0$ with $k_3[IH] \ll k_2[RH]$ and $\delta_0 \ll 1$, we obtain

$$-\frac{d[IH]}{dt} = \left[1 + \frac{\alpha k_3}{k_6 - \delta k_2 [RH] - \delta_0 k_2 [RH]/[IH]}\right] k_0 [IH][O_2]. \quad (85)$$

This formula can be transformed into

$$-\frac{di}{d\theta} = \frac{i^2}{i-1} + \frac{k_3 - \delta_i k_2 [RH]}{k_2}, \quad (86)$$

where

$$i = [IH]/[IH]_{cr} \text{ и } \theta = \alpha k_0 k_3 [O_2] t/(k_3 - \delta_i k_2 [RH])$$

are dimensionless coordinates (of inhibitor concentration and time). If α is large, while the difference $k_3 - \delta_i k_2[RH]$ is small, the last term in (86) can be neglected, and the concentration dependence of the rate of inhibitor consumption becomes

$$-di/d\theta = i^2(i-1)^{-1}. \quad (86a)$$

Fig.16 shows that, despite the complicated concentration dependence of the rate of inhibitor consumption indicated by formula (86a), the minimum lies high above the abscissae axis, so that the rate departs little from its mean value, by not more than 20% over the range $i = 1.3$–4.7, and even 5.6% in the range 1.5–3. In conformity with this the variation in the concentration of antioxidant of moderate strength is nearly linear in the region of the critical concentration. Experimental curves for the consumption of many inhibitors, e.g. phenyl-2-naphthylamine[101] (Fig.17), are similar in form to the calculated curves in Fig.16.

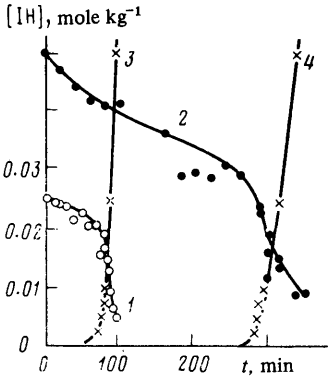


Figure 17. Inhibited oxidation of polypropylene[101] under 300 mmHg of oxygen at 200 °C: *1*) variation in concentration of phenyl-2-naphthylamine (initial concentration 0.025 mole kg^{-1}); *2*) as (*1*) but initially 0.05 mole kg^{-1}; *3*) absorption of oxygen (0.025); *4*) absorption of oxygen (0.05).

Equation (82) has no real roots, i.e. the inhibitor has no critical concentration, when

$$\delta_i > (1 - \delta_0^{1/2})^2 k_3/k_2[RH]$$

such an inhibitor cannot make oxidation a stationary process whatever its concentration: i.e. it is a weak antioxidant. Equations (75) cannot then be solved by Bodenstein's method. The autocatalysis factor for oxidation of a polymer in the presence of a weak antioxidant can be determined by means of Semenov's formula[107]

$$\varphi = (\nu\delta - 1)/\theta, \quad (87)$$

in which ν is the length of the unbranched chain, in the present case

$$\nu = 1 + k_2[RH]/k_3[IH], \quad (88)$$

and θ the lifetime of the branching product, i.e. $\theta = (k_4[RH])^{-1}$ when $[R_2S] = 0$. Substituting in (87) for δ from (74) and for ν from (88), we find that

$$\varphi = \frac{k_4[RH]}{k_2}\left\{\delta_i k_2[RH] - (1-\delta_0)k_3 + \delta_i k_3[IH] + \frac{\delta_0 k_2[RH]}{[IH]}\right\}. \quad (89)$$

The expression in braces is the left-hand side of (82) divided by [IH], and with

$$\delta_i > (1 - \delta_0^{1/2})^2 k_3/k_2[RH]$$

is positive at all values of [IH]. For certain mean values of [IH] both terms containing it in the brackets in Eqn.(89) can be neglected. Over this concentration range the rate of absorption of oxygen and of other stages in oxidation of a

polymer containing a weak antioxidant will be described by the exponential law $w = w_0 \exp(\phi t)$ with ϕ constant.

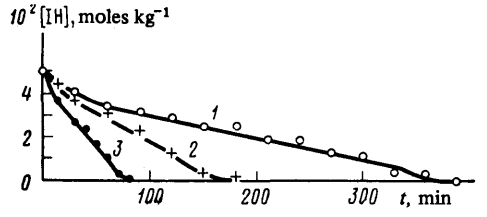


Figure 18. Variation in concentration of the weak antioxidant 2,6-di-t-butyl-4-phenylphenol during induction period in the oxidation of polypropylene under 300 mmHg of oxygen at (°C): *1*) 180; *2*) 190; *3*) 200.

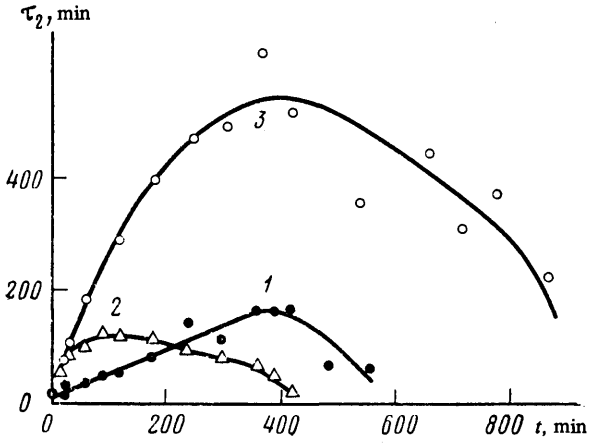


Figure 19. Dependence of induction period in the oxidation of polypropylene containing conversion products of antioxidants (unconsumed antioxidants removed by vaccum distillation at 200 °C) on duration of oxidation of initial specimens[80] under 300 mmHg of oxygen at 200 °C for additions of a mixture of inhibitor (I) (0.16 mole kg^{-1}) with: *1*) didecyl sulphide; *2*) inhibitor (II) (0.08 mole kg^{-1}); *3*) a mixture of (II) and didecyl sulphide (each 0.08 mole kg^{-1}).

The rate of consumption of inhibitors that are weak antioxidants considerably exceeds that of strong antioxidants. The proportion of direct oxidation of the inhibitor is then insignificant in comparison with its consumption in chain termination, the rate of which is given approximately by the product of the instantaneous inhibitor concentration and a quantity proportional to exp ϕt. The curves described by this law are sometimes fairly complicated, but sometimes they approximate to straight lines[108,109] (Fig.18).

So far we have been considering only the action of the initial inhibitor. However, conversion products of inhibitors are usually involved in oxidation of a polymer, and are quite often fairly effective antioxidants. The conversion products remaining in a polymer after unconsumed inhibitor has been removed from it may ensure long induction periods (Fig.19).[80] Formula (81) shows that a weak inhibitor, in whose presence the critical concentration increases right up to $\delta = 1$, may behave as a strong antioxidant in the presence of a sufficient concentration of a reductant for hydroperoxide.

When a polymer contains both a weak or moderate antioxidant and a hydroperoxide reductant at a constant total concentration $[A] = [IH] + [R_2S]$, substitution in (81) of $\delta = \delta_0 + \delta_i[IH]$ and $[R_2S] = [A] - [IH]$, with neglect of $k_3[IH]$ in comparison with $k_2[RH]$, yields for the critical inhibitor concentration

$$[IH]_{cr}^2 - \left\{\frac{k_4[RH]}{k_3 k_6}(k_3 - \delta_i k_2 [RH]) + [A]\right\}[IH]_{cr} + \frac{\delta_0 k_2 k_4}{k_3 k_5}[RH]^2 = 0. \quad (90)$$

This quadratic equation has two positive real roots provided that [A] exceeds some critical value

$$[A]_{cr} = \frac{k_4[RH]}{k_3 k_5}(\delta k_2 [RH] - k_3) + 2[RH](\delta_0 k_2 k_4 / k_3 k_5)^{1/2}. \quad (91)$$

Thus for every concentration $[A] > [A]_{cr}$ there exist two critical mixture compositions such that only between them is oxidation a stationary process, but outside this range it is autocatalytic. On plots of induction period against composition short induction periods correspond to an autocatalytic process, but long induction periods to a steady-state process. If one of the mixture components is an antioxidant of medium strength, having a critical concentration even in the absence of a reductant, the region of a steady-state process will adjoin the edge of the diagram provided that $[A] > [IH]_{cr}$.

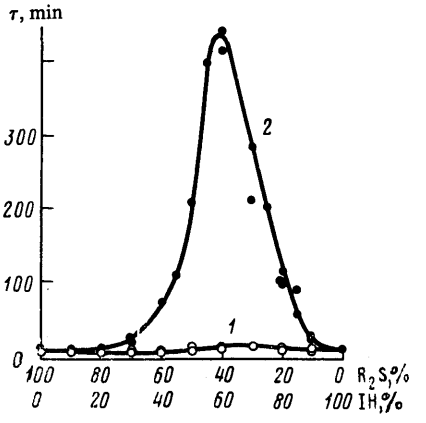


Figure 20. Dependence of induction period τ in the oxidation of polypropylene under 300 mmHg of oxygen at 200 °C on composition of a mixture of phenyl-2-naphthylamine (IH) and didodecyl thiodipropionate (R_2S) [97] at total concentrations (mole kg^{-1}): *1*) 0.005; *2*) 0.010.

Fig.20 shows such plots for two mixture concentrations lying below and above the critical total $[A]_{cr}$. It is evident that doubling the total concentration produces a sharp change in the character of the diagram, with appearance of a narrow maximum[97]. Many similar diagrams have been published[80,109,110].

The above phenomenon, consisting in the longer or more effective inhibition of oxidation by a mixture of two antioxidants than by each component at a specified total concentration, is termed *antioxidant synergism*. The only rigorous criterion of synergism may be the presence of a maximum in the composition dependence of induction period or of a minimum in that of rate of degradation. From a practical point of view it is advantageous to replace an individual antioxidant by a mixture only if the mixture at a constant total concentration (or a constant total cost) retards oxidation longer or more effectively than does each component, whence follows the above definition of synergism.

In some cases a mixture of two antioxidants is less effective than the more effective component at the same partial concentration, a phenomenon that is termed *antioxidant antagonism*. An example of such antagonism was illustrated in Fig. 10. We shall examine another example in greater detail.

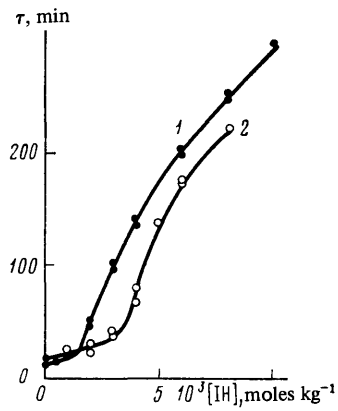


Figure 21. Effect of 2,4,6-tri-t-butylphenol (0.01 mole kg^{-1}) on dependence of induction period in the oxidation of polypropylene under 300 mmHg at 200 °C on the concentration of methylene-2,2′-bis-(4-methyl-6-t-butylphenol)[108]: *1*) second inhibitor absent; *2*) second inhibitor present.

In Fig. 21 the curve representing the dependence of the induction period in the oxidation of polypropylene, containing the weak antioxidant 2,4,6-tri-t-butylphenol at a constant concentration of 0.01 mole kg^{-1}, on the concentration of a second antioxidant (II) lies below the corresponding curve for pure polypropylene almost throughout its length[108], and the partial critical concentration of the strong antioxidant (II) is increased in the presence of weak 2,4,6-tri-t-butylphenol. Assuming that both antioxidants (IH′ and IH″) terminate chains, replacing $k_3[IH]$ in (81) by $k_{31}[IH'] + k_{32}[IH'']$, and rearranging ($[R_2S] = 0$), we obtain

$$[IH']_{cr} = \frac{\delta k_2 [RH]}{(1-\delta) k_{31}} - \frac{k_{32}}{k_{31}} [IH''] . \qquad (92)$$

Differentiating (92) with respect to [IH″], we then find that

$$\frac{\partial [IH']_{cr}}{\partial [IH'']} = \frac{k_2 [RH]}{(1-\delta)^2 k_3} \cdot \frac{\partial \delta}{\partial [IH'']} - \frac{k_{32}}{k_{31}} \qquad (93)$$

will be positive (i.e. the critical concentration of IH′ will increase in the presence of IH″) only if the second antioxidant increases the probability of degenerate chain branching sufficiently strongly, so that

$$\frac{\partial \delta}{\partial [IH'']} \cdot \frac{k_{32} (1-\delta)^2}{k_2 [RH]} > 0. \qquad (94)$$

Hence in this case the antagonism is explained by a marked increase in the probability of chain branching under the influence of the second antioxidant: mixtures of two inhibitors—one strong and the other a weak antioxidant—may in some cases be less effective than one of the components (the strong antioxidant) used separately at the same concentration as in the mixture.

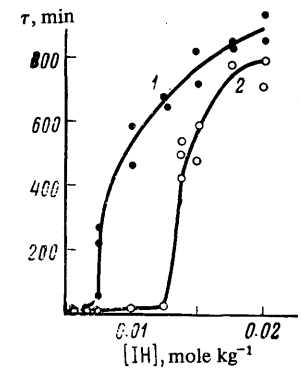


Figure 22. Effect of mixing of inhibitor with polymer on dependence of induction period in the oxidation of polypropylene under 300 mmHg at 200 °C on concentration of dimethylbis-*p*-aminophenylphenoxysilane[111]: *1*) non-uniform; *2*) uniform.

Diminished efficiency of an antioxidant may be due to insufficiently uniform admixture with the polymer. Thus a threefold increase in the "inoperative" concentration of the antioxidant dimethylbis-*p*-phenylaminophenoxysilane was observed[111] on passing from a uniform to a non-uniform distribution (polypropylene powder consisting of spherical particles of mean diameter 0.03 mm moistened with a benzene solution of the antioxidant and dried at room temperature) (Fig. 22).

A theory has been developed for the oxidation of a non-uniformly inhibited polymer[112]. Calculations were based on a simplified scheme for the progress of a branched chain reaction involving active centres of a single type. The variation in concentrations of active centres and inhibitor n and i during such reaction can be described by the equations[100]

$$dn/dt = w_0 + \varphi n - kin, \qquad (95)$$

$$-di/dt = kin, \qquad (96)$$

in which ϕ is the autocatalytic factor, w_0 the rate of chain generation, and k the rate constant of chain termination by the inhibitor. The critical inhibitor concentration in the reaction is $i_{cr} = \phi/k$. Progress of the reaction is autocatalytic or stationary according as $i < i_{cr}$ or $i > i_{cr}$.

For an extended non-uniformly inhibited specimen we must take into account the redistribution of inhibitor and active centres resulting from diffusion, for which purpose we introduce appropriate terms[113] into Eqns.(95) and (96):

$$\partial n/\partial t = D\partial^2 n/\partial x^2 + w_0 + \varphi n - kin, \qquad (95a)$$

$$\partial i/\partial t = D_i\partial^2 i/\partial x^2 - kin, \qquad (96a)$$

where D and D_i are the diffusion coefficients of active centres and of inhibitor, while x is the coordinate. In the oxidation of a long unidimensional specimen[112] part of which ($0 \leq x < x_1$) is devoid of inhibitor, while the remainder contains inhibitor at a constant concentration i_2, the initial concentration of active centres throughout the specimen equals their steady-state concentration in the inhibited portion:

$$n_0 = w_0/(ki_2 - \varphi).$$

The set of equations was integrated on a computer after transformation into

$$\partial N/\partial\tau = \gamma\partial^2 N/\partial z^2 + N(1-I) + (I_2 - 1), \qquad (97)$$

$$\partial I/\partial\tau = \partial^2 I/\partial z^2 - AIN. \qquad (98)$$

Here N and I are dimensionless concentrations corresponding to n and i, while z and τ are the dimensionless coordinate and time:

$$dz = (\varphi/D_i)^{1/2}dx;\ d\tau = \varphi dt;\ N = n/n_0;\ I = ki/\varphi = i/i_{cr}.$$

The coefficients are given by $A = kn_0/\phi$ and $\gamma = D/D_i$. Calculations were based on $A = 10^{-3}$, $\gamma = 1$, a uniform initial distribution of active centres ($N = 1$), and a non-uniform distribution of inhibitor ($I = 0$ for $0 \leq z < z_1$, and $I = I_2$ for $z \geq z_1$). Solutions of Eqns.(97) and (98) are illustrated in Fig.23.

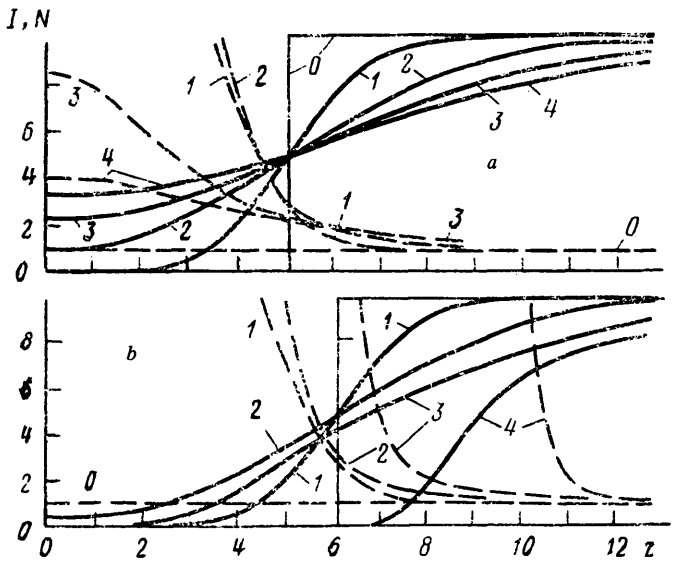


Figure 23. Distributions of dimensionless concentrations of inhibitor and active centres I and N in a unidimensional specimen[112] ($\gamma = 1$; $I_2 = 10$) for different values of z_1: *a*) 5.125; *b*) 6.15 at different times θ during the process: *0*) 0; *1*) 1; *2*) 5; *3a*) 10; *3b*) 12.5; *4a*) 15; *4b*) 17.5.

Fig.23 shows the distributions of dimensionless concentrations of inhibitor and active centres in specimens differing in the size of the initially uninhibited portion z_1. At first the process develops similarly in the two cases: both N and I increase in the originally uninhibited segment. After some time, however, a difference appears: if $z_1 = 5.125$ the concentration I increases monotonically throughout the range $0 \leq z < z_1$, but N begins to decrease: i.e. the process that began in the uninhibited portion of the specimen dies away. With $z_1 = 6.15$, on the other hand, I begins to decrease after some time, whereas N continues to increase. A reaction front appears: within a relatively narrow range of change in z the concentration I changes from approximately zero on the left to more than unity on the right, while N drops sharply in the same interval. The reaction front gradually moves to the right, towards larger z. There thus exists a limiting size of the originally uninhibited region such that, if the actual size is smaller, the process therein dies out; but if the portion free from inhibitor is larger than the critical size, a stable region of rapid oxidation arises, which spreads throughout the specimen.

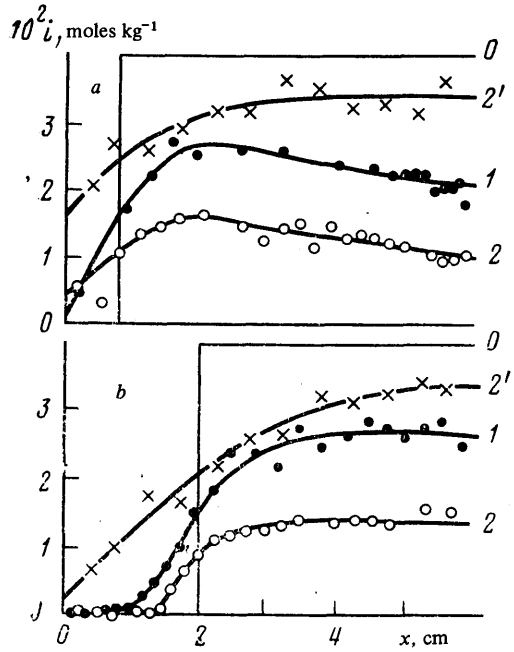


Figure 24. Concentration distribution of inhibitor methylene-2,2'-bis-(4-methyl-6-t-butylphenol) along specimen of atactic polypropylene[114] under an oxygen partial pressure of 150 mmHg (air) at 190 °C for different lengths x_1 (cm) of initially uninhibited region: *a*) 0.8; *b*) 2.0 after different periods of oxidation (min): *0*) 0; *1*) 150; *2*) 300; *2'*) 300, distribution of radioactive inhibitor and conversion products when labelled inhibitor used.

Fig.24 shows the concentration distribution of the inhibitor methylene-2,2'-bis-(4-methyl-6-t-butylphenol) (II) 150 and 300 min after the start of oxidation (in air at 190 °C) of specimens of atactic polypropylene having the non-uniform

initial inhibitor distribution shown by the broken lines 0. If the section devoid of inhibitor is 0.8 cm long, after some time inhibitor penetrates the left-hand (uninhibited) portion, suppressing oxidation. If the uninhibited portion is 2.0 cm long, inhibitor is not detected in the left-hand section, although in both cases conversion products of the inhibitor penetrate the specimen to the very edge ($z = 0$). After oxidation for 300 min the inhibitor-free portion becomes larger than it had been at 150 min. Apart from certain details, such as the maximum in the inhibitor distribution curves in Fig. 24*a* due to enhancement of its solubility in the slightly oxidised polymer and the greater rate of consumption of inhibitor in the right-hand portion (Figs. 23 and 24), calculation and experiment almost coincide[114,115].

Almost all the above experimental results relate to the oxidation of polypropylene, since systematic data have not appeared for other polymers. Passing from one polymer to another involves changes primarily in ease of detachment of the hydrogen atom from the monomer unit RH, in the distances between them, and in the solubility of oxygen: i.e. the rate constants k_0, k_1, k_2, and k_4, those of quadratic chain termination, and also the yields of hydroperoxide α and those of radicals on its breakdown δ are affected. Changes in these parameters entail changes in the rates both of uninhibited and of inhibited oxidation.

As mentioned above, inhibitors retard oxidation by interacting with peroxy-radicals $RO_2^{\cdot}$. The reactivity of such radicals is little dependent on the structure of the residue R, which is remote from the reaction centre. The rate of chain termination, i.e. the rate of interaction of $RO_2^{\cdot}$ radicals with inhibitor molecules, depends not only on the reactivity of the reactant species but also on the number of collisions between them, i.e. on concentrations and diffusion coefficients.

If a polymer contains functional groups capable of forming complexes with inhibitor molecules

$$IH + X{-}R \rightleftharpoons IH \cdot X{-}R, \qquad (99)$$

the concentration of mobile inhibitor molecules not bound in complexes will form only part its total concentration in the polymer [IH]. In the simplest case, when $[IH] \ll [IH]_p$ and $[IH]_p \ll [X{-}R]$, we obtain

$$[IH] \text{ moles kg}^{-1} = \frac{[IH \cdot XR]}{k\,[X{-}R]} = \frac{m\,[IH]_p}{1000kn}, \qquad (100)$$

where m is the equivalent weight of a monomer unit and n the number of functional groups in a unit that are involved in complex formation. Under otherwise similar conditions the effective rate constant of chain termination by an inhibitor that forms complexes with particular functional groups in the polymer will be smaller than the corresponding rate constant for an inhibitor that is incapable of complex formation. This apparently explains the relative ineffectiveness of phenolic inhibitors in polyamides[116].

Inhibitor molecules can be retained not only by polar groups but also by sites of disorder in the relative arrangement of macromolecules[117]. The sorption capacity of a polyalkene, i.e. the number of sites capable of retaining simple substances, can be increased by special treatment of the melt[118–120]. Enhancement of sorption capacity leads to some increase in the critical concentration of the inhibitor accompanied by decrease in the rate of its consumption, which at high inhibitor concentrations may lengthen the time during which it operates.

With a given polymer in the solid state the parameters k and i_{cr} in formula (66) for a particular inhibitor depend on the temperature–time conditions of preparation of the specimen[121,122]. Good compatibility of inhibitor with polymer diminishes the effectiveness of the former[123]. Compatibility was measured[123] by the rate of vaporisation of the inhibitor from the polymer, a quantity proportional to the concentration of mobile (not sorbed at any centres) inhibitor molecules.

The rate of inhibited oxidation increases[124,125] on passing from a homopolymer of ethylene to copolymers with propylene and with vinyl chloride. Both parameters in Eqn. (66), k and i_{cr}, increase, passing through maxima at certain contents of the foreign units. These parameters increase also with the γ-ray dosage of polyethylene[126]. Any breakdown in order of arrangement of macromolecules probably diminishes the stability of the polymer.

VI. SOME SPECIAL METHODS FOR THE STABILISATION OF POLYMERS

All known antioxidants rapidly become less effective with rise in temperature, and all the usual antioxidants cease to retard the oxidation of polymers between 270 and 300 °C. However, oxidation can be slowed down even at high temperatures.

A polymer can be protected from oxidation under processing conditions by conducting the operation in an inert atmosphere (nitrogen, carbon dioxide). In small-scale production an inert atmosphere can be produced in a closed space by the use of absorbents for oxygen, but these cannot protect the polymer from oxidation during storage and use[127]. To estimate the time during which such an absorbent acts we take the diffusion coefficient of molecular oxygen in the polymer at room temperature to be 10^{-6} cm^2 s^{-1},[128] and the solubility coefficient to be 0.02 mole kg^{-1} atm^{-1}. In air ($p_{O_2} = 0.2$ atm) the concentration of oxygen at the polymer surface will be 4 mmoles kg^{-1} or 4 μmoles cm^{-3}. If all the oxygen is absorbed in a layer 0.1 cm thick, its flow through 1 cm^2 of surface will be at least 40 pmoles cm^{-2} s^{-1}; and if the absorbent concentration is 0.1 mole kg^{-1} or 10 μmoles cm^{-2} in the 0.1-cm layer, the absorbent will be exhausted in 2.5×10^5 s or 3 days. This time will become shorter with rise in temperature.

One consequence of thermo-oxidative degradation is the formation of volatile products, some of which may be toxic[129]. Special absorbents are introduced into polymers to eliminate this effect. Thus barium, lead, or other salts of weak organic acids are added to absorb hydrogen chloride formed on the degradation of poly(vinyl chloride)[130]; polyamides are added to absorb formaldehyde formed in the oxidative degradation of polyoxymethylene; etc.

Discoloration during the oxidation of polymers is due to formation of a system of conjugated bonds. Substances capable of adding to such bonds will weaken the effect[130].

Every new component introduced into a polymer, either by chance or deliberately, influences the resistance of the latter to thermo-oxidative degradation. Thus metals of variable valency increase the yield of free radicals formed by the breakdown of hydroperoxides. This effect can be lessened by introducing into the polymer complexing agents, in particular ethylenediaminetetra-acetic acid and its derivatives[130].

The widely used colorant, filler, and photostabiliser—carbon black—protects a polymer from thermal oxidation at not very high temperatures, but catalyses the oxidation of many stabilisers at processing temperatures[131,132]. Polymers containing carbon black are protected by the use of thiophenols[131,132] and other sulphur derivatives[130].

At present no general methods are available for combating the harmful effects of impurities.

Thus intense research on the ageing and stabilisation of polymers has not yet eliminated the empirical selection of

stabilisers for specific polymer materials. However, from the time of the first investigations in this field the range of compounds among which effective stabilisers must be sought has been continually narrowed down, and the synthesis of novel stabilisers has become increasingly selective. In some cases the concept of critical concentrations has permitted prediction of the effects of mixing two antioxidants differing in structure. Among problems that remain unsolved in the stabilisation of polymers the first task is to develop methods for retarding oxidation at temperatures above 300 °C.

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Alkaline-earth Metals and Compounds as Initiators of the Anionic Polymerisation of Unsaturated Monomers

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Data on the catalytic activity and stereospecificity of alkaline-earth metals in the polymerisation and copolymerisation of unsaturated monomers are summarised, and the nature of the active centres is examined togeher with the kinetics and the mechanism of these processes. The principal methods of preparing initiators for anionic polymerisation that contain compounds of these metals are outlined, and the most probable immediate prospects for practical application of the compounds in polymerisation processes are noted. A list of 175 references is included.

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I. INTRODUCTION

The first publications on the ability of organolithium compounds to initiate the formation of *cis*-1,4-polyisoprene, similar in structure and properties to natural rubber[1,2], and the series of papers by Szwarc began at about the same time, which first directed attention to several unusual and interesting properties of living polymers[3-5], led to a sharp growth of interest in anionic polymerisation. During the past two decades great progress has been made both in the theory of processes initiated by alkali metals and in their practical realisation, thanks to which they now find widespread industrial application in the manufacture of various synthetic polymer materials[6]. Research on processes involving alkaline-earth metals has hitherto developed far more slowly, which is largely due to difficulties in the preparation of appropriate polymerisation initiators.

The first systematic studies in this field[7,8] were made with organocalcium compounds, which were more accessible at that time; but subsequently attention was focussed mainly on barium compounds, which exhibited interesting catalytic properties in the polymerisation and copolymerisation of diene monomers[9-12]. Sufficient information has now been obtained for the possible formulation of several general rules in this independent new field in the theory of anionic polymerisation and for identification of the most promising practical aspects.

The present Review is devoted to the polymerisation of unsaturated polymers initiated by calcium, strontium, barium, and their compounds. Magnesium compounds are included only where necessary for comparison and for citing fundamentally novel results not covered by previous reviews[13,14].

The Review begins with an outline of methods for preparing the chief polymerisation initiators containing compounds of alkaline-earth metals that are used at the present time, since most of this information has been obtained recently and has not appeared in the well known monographs on the preparation of organometallic compounds[15,16].

II. PRINCIPAL METHODS FOR THE PREPARATION OF POLYMERISATION INITIATORS BASED ON COMPOUNDS OF ALKALINE-EARTH METALS

Organometallic compounds are usually formed considerably more readily in the presence of electron-donor solvents, whereas the presence even of catalytic quantities of polar compounds is in many cases sufficient to change appreciably the character of anionic polymerisation processes and also the structure and properties of the resulting polymers[17-19]. Therefore chemists investigating polymerisation tend to prepare the initiator in the solvent in which subsequent polymerisation is to be conducted. Workers studying the polymerisation of diene monomers display a special interest in hydrocarbon solvents, which show the greatest practical promise with respect both to the properties of the resulting polymers and to technical and economic factors.

1. Electron Transfer to Hydrocarbons

Alkaline-earth metals are considerably less active than alkali metals in reactions involving electron transfer to aromatic compounds. Only in polar solvents of high solvating power such as hexamethylphosphorotriamide do they form compounds comparatively readily with biphenyl, naphthalene, anthracene, 1,1-diphenylethylene, and similar compounds[20-22]. In reactions of this type calcium is considerably less active than are magnesium and barium[22,23], which as with alkali metals[18,24] is due to competition between two main factors governing the activity of metals in these processes—the tendency to donate electrons and the gain in energy of solvation of the cation—which vary in opposite directions within a given group.

In ethereal solvents only the higher fused hydrocarbons (naphthacene, perylene), among aromatic compounds, react with alkaline-earth metals, forming sparingly soluble radical-anions and dianions that are inert towards polymerisation[23,25].

The addition of barium to non-polymerising 1,1-disubstituted vinylated aromatic compounds—1,1-diphenylethylene or α-methylstyrene—proceeds considerably more readily[10,26-28]. The products are probably metal salts of dianions—of the dimer of diphenylethylene $ba^{+-}C(C_6H_5)_2.CH_2.CH_2.C(C_6H_5)_2C^-ba^+$ (where ba is an equivalent of barium) or an oligomer of α-methylstyrene—like the well studied alkali-metal compounds[10]. Formation of the corresponding barium derivatives of oligomeric dianions of styrene (degree of polymerisation 2–5) has also been reported recently[29], but in this case special measures are necessary to prevent homopolymerisation of styrene.

Formation of all these products involves recombination of primary monomeric radical-anions[18], which is responsible for the difunctionality of the product and also increases their yield significantly, despite the relatively low electron affinity of the initial hydrocarbons.

It has recently been reported[30] that depending on the conditions the action of barium on α-methylstyrene in oxolan yields either dianions of the above type or products having only one active end. As single-ended products had never previously been observed in such systems and their formation is difficult to understand, it is not yet clear whether their appearance is a specific feature of barium or whether it is due to experimental error.

Bis-1,1,4,4-tetraphenylbutylbarium has been characterised by spectroscopic and conductivity methods[31-33]. Together with its α-methylstyrene analogue it is now probably the simplest (with regard to preparation) and most often used organobarium polymerisation initiator. Similar compounds have been obtained with strontium[34,35]; in the cases of calcium and magnesium, reaction with 1,1-diphenylethylene in ethereal media is insignificant if it occurs at all[23,26].

The reaction of alkaline-earth metals with hexa-arylethanes is apparently of the same type; it occurs readily in oxolan at room temperature and yields bistriarylmethyl derivatives of the metals[36,37]. Addition products of calcium, strontium, and barium with benzophenone (ketyls) have also been obtained in oxolan[38,39]; they initiate the polymerisation of acrylates[39], but are apparently inactive in the polymerisation of hydrocarbon monomers[40].

It has recently been shown[174] that in aromatic hydrocarbons at 50–80 °C hexaphenylethane reacts with metallic barium and strontium to form the corresponding bistriphenylmethyl derivatives, which are soluble in the reaction medium. This is the first known example of the synthesis of completely substituted compounds of alkaline-earth metals in the absence of solvating agents.

2. Reaction with Halogenohydrocarbons

Organic derivatives of alkaline-earth metals were first obtained in this way—phenylcalcium iodide in 1905,[41] phenylbarium iodide in 1927 [42]—but after it was early established that difficulties were involved in synthesis and that the products were unpromising in preparative chemistry compared with Grignard reagents, interest in this reaction died away for a long time, and was renewed only in the 1960s [43] (the history and the present-day achievements of this method have been covered quite fully in Ref. 44). Quite a number of publications have now appeared on the preparation of compounds of type RCaX (in which X is most often iodine, more rarely bromine or chlorine) in oxolan or diethyl ether[45-50]. If the metal used is especially pure, the reaction can be conducted even in a hydrocarbon medium[51] (though insoluble products are then formed, which hinders their further application). Compounds of strontium[36,52-54] and of barium[36,52,53,55] have been obtained by this method in ethereal media. With these two metals the preparation could not be effected in a hydrocarbon medium, but compounds of calcium, strontium, and barium have been obtained by cocondensation of metal and halogenoalkane vapours on a cooled surface in the absence of a solvent[53].

The substances obtained by this reaction are mixtures of completely and incompletely substituted compounds (R_2M + RMX), whose composition depends both on the nature of the alkyl halide and on the reaction conditions[9,50,56]. On the whole this method, though the principal route to lithium initiators, has not yet found appreciable extension to the synthesis of polymers in the case of alkaline-earth metals.

3. Dimetal Compounds

Alkaline-earth metals on reaction with excess of diethylzinc in benzene[57] fairly readily form dimetal complexes of general formula $MZn(C_2H_5)_4$. Such compounds were used by Furukawa et al. for the polymerisation of certain polar monomers[58,59], but they were relatively inactive owing to their insolubility and their complicated composition. At the beginning of the 1970s interest was renewed in organometallic derivatives containing both barium and zinc, as they exhibited interesting catalytic properties in the polymerisation and copolymerisation of dienes[9,11,12,60]. Methods were found for obtaining hydrocarbon-soluble initiators, which could be readily separated from excess of metal and other impurities by conducting the preparation in the presence of 1,1-diphenylethylene[61] or by replacing diethylzinc with dibutylzinc[12,62] (in the latter case there are grounds for supposing that the initiator is formed in diethyl ether[63]). Opportunities for the wider application of these compounds apparently depend on the availability of zinc alkyls.

Analogous aluminium complexes of general formula $M(AlR_4)_2$ have recently attracted attention. They are formed from the trialkylaluminium and the alkaline-earth metal[61,64] or an alkoxide thereof[65,66]. They are readily soluble in benzene and effect the polymerisation of hydrocarbon monomers, although considerably less active than zinc complexes[61].

4. Other Methods

Completely substituted organic derivatives of calcium, strontium, and barium are readily formed in oxolan from the corresponding compounds of mercury[67-70] and also (under more severe conditions) of lead[71] and tin[72]. Organomercuric synthetic reactions and the properties of the compounds isolated—including infrared, ultraviolet, and nuclear magnetic resonance spectra of several compounds—have been described most fully in patents of the Dow Chemical Co.[68]; compounds containing radicals with conjugated bonds (allyl, phenyl, benzyl, indenyl, etc.) can be obtained more readily.

Hydrocarbons containing a mobile hydrogen atom—such as fluorene, triphenylmethane, indene, cyclopentadiene, phenylacetylene—have been metallated by the action of alkaline-earth metals in strongly solvating media (liquid ammonia[73,74], hexamethylphosphorotriamide[75], 1,1-dimethyl ethylene[75], methylamine[76]). Fluorenylstrontium[77,78] and fluorenylbarium[78-81] have been obtained also by the metallation of fluorene with 1,1,4,4-tetraphenylbutyl derivatives of the metals in oxolan. However, compounds containing mobile, readily substituted hydrogen (fluorene, cyclopentadiene, etc.) form stable carbanions, which are relatively inactive in the polymerisation of hydrocarbon monomers[18,82,83].

Cumenylstrontium and cumenylbarium can be obtained[84] by cleaving cumenyl methyl ether with dispersion of the metals in oxolan.

Exchange reactions have recently been observed between barium alkoxides and organomagnesium (and organolithium) compounds[85-87], similar to those between lithium alkyls and sodium (and potassium) alkoxides[88]. The products apparently contain varying proportions of symmetrical and unsymmetrical compounds R_2Ba and RBaOR', with a significant influence on their catalytic properties[86]. Various systems of this type have been described in the patent literature[89-91]. Numerous multicomponent systems, representing various combinations of the above variants, have also been suggested (e.g. calcium–anthracene–trialkylaluminium[92], barium or strontium acetylacetonate–trialkylaluminium–alkyl–lithium[93], barium alkoxide–lithium alkoxide–trialkylaluminium[94]).

Thus the preparation of organic derivatives of alkaline-earth metals in the presence of highly polar solvents such as hexamethylphosphorotriamide presents no difficulty, but the products hardly differ in catalytic properties from the more readily available alkali-metal compounds. In ethereal solvents (oxolan, dimethyl ether) compounds having two active ends, such as bistetraphenylbutyl-barium and -strontium, are most simply obtained. The most reliable method for obtaining compounds that are completely substituted with hydrocarbon radicals having one active end is apparently reaction with mercury compounds or with hexaphenylethane.

In hydrocarbon media completely substituted compounds (bistriphenylmethyl-barium and -strontium) have been obtained only recently, as mentioned above. Several workers[9,95-97] have therefore used initiators obtained in ethereal media by removing the electron donor under more or less severe conditions. With such a method, of course, doubt always remains whether the solvent has been completely removed. The possibility of almost complete removal of oxolan has until now been confirmed analytically only for barium compounds[98].

Furthermore, as many workers have shown[51-53,68,87], the lower alkyl compounds of alkaline-earth metals are thermally unstable at room temperature, and also decompose under the influence of oxolan and other ethereal solvents. Dibenzylbarium in oxolan also undergoes gradual deactivation and isomerisation[70]. On the other hand, compounds having branched carbanions of the di- and tri-phenylmethyl type are completely stable both in hydrocarbon and in ethereal media[32]. Therefore the introduction of 1,1-diphenylethylene (sometimes α-methylstyrene) into the reaction system is often a useful method for improving the stability and the solubility of the resulting organometallic compounds[69,85,97].

III. CATALYTIC ACTIVITY AND STEREOSPECIFICITY OF ALKALINE-EARTH METALS IN POLYMERISATION PROCESSES

1. General Behaviour

The first investigations on polymerisation involving calcium, strontium, and barium used the free metals as initiators[99-105], but in most cases the results showed considerable scatter. Satisfactory reproducibility was subsequently obtained with respect to the structure of the polymers and the composition of copolymers[10,106,107], but recently almost all studies have been made under homogeneous conditions, as a consequence of the progress made in preparing compounds of these metals.

By now most monomers capable of anionic polymerisation—unsaturated compounds containing conjugated double bonds or polar substituents, such as dienes, styrene, methyl methacrylate—have been subjected to polymerisation initiated by alkaline-earth metals and their compounds. Acrylonitrile and vinyl chloride have been polymerised by the action of a dispersion of barium[100] (under homogeneous conditions, the latter could not be polymerised by an organobarium initiator[108]).

Monomers having polar side-groups are readily polymerised by the action of magnesium compounds[13,14]. Reaction of hydrocarbon monomers requires either the presence of such strong solvating agents as hexamethylphosphorotriamide[13,21,109,110] or magnesium alkoxides of certain ether–alcohols, e.g. methylcellulose or oxolan-2-ylmethanol[111,112], or (slowly) heating to 80–100 °C.[113,114]

It is interesting that metallic magnesium, which is fairly active in electron-transfer processes, reacts comparatively readily in ethereal solvents with butadiene[115-117], isoprene[118], and also with styrene and several other unsaturated compounds[119]. Since the organomagnesium compounds thus formed do not polymerise these monomers, the reaction ceases at the stage of the primary oligomeric products, and can be used to obtain concentrated solutions of double-ended organomagnesium compounds.

In the early work, concerned mainly with the polymerisation and copolymerisation of methyl methacrylate under the influence of dispersions of alkaline-earth metals, doubts were expressed concerning the mechanism of these processes: in particular it was suggested that not only an anionic but also a radical process took place[106,120-122]. The chief arguments supporting this hypothesis were the presence of a certain quantity of styrene and its copolymer with methyl methacrylate and also the difference in the general rules of stereoregulation from those found previously for reactions with alkali metals. A relevant fact here is that it has been shown many times with alkali metals that the styrene–methyl methacrylate pair cannot be used to establish the mechanism of heterogeneous processes, since in this case polymerisation is initiated predominantly on the styrene as a consequence of its considerably stronger adsorption on the metal surface[18,123]. At the present time no doubt arises about the anionic mechanism of polymerisation processes initiated by alkaline-earth metals, and the differences (sometimes very substantial) observed from processes with alkali metals reflect differences in the properties of active centres with uni- and bi-valent gegenions.

2. Stereospecificity of Alkaline-earth Metals

(a) Diene monomers

The most complete and reliable information has been obtained for the polymerisation of butadiene. The laws thus found (Table 1) differ in many respects from those established previously for alkali metals.

Hydrocarbon medium. Firstly it is evident that in hydrocarbon media metals of Group II possess a considerably greater ability than the corresponding metals of Group I to cause the 1,4-addition of butadiene units. Moreover, the total content of 1,4-units in butadiene polymers formed by the action of any alkaline-earth metal approaches those obtained in the presence of lithium, which has hitherto occupied an exceptional position among initiators of anionic polymerisation. In its ability to form a *cis*-1,4-butadiene structure barium surpasses all other initiators based on non-transition metals, including lithium (at very low concentrations of active centres ($\sim 10^{-5}$ M) the content of *cis*-1,4-units in lithium-polybutadiene obtained in an aliphatic solvent may reach 80–85%[128]). When the temperature is raised to

95 °C however, the content of *cis*-1,4-butadiene units in polymers obtained by using barium falls to 42% (with a constant content of 1,2-units[129]); for comparison the content of *cis*-1,4-units when polymerisation is effected by using lithium remains almost unchanged between −20 and 196 °C.[130]

Table 1. Structure of butadiene polymers formed at room temperature by means of initiators based on metals in Groups I and II.

Initiator	Content of monomer units, %			Ref.
	cis-1,4	*trans*-1,4	1,2	
hydrocarbon medium				
RLi	43	50	7	[17]
Na	23	45	32	[17]
K	16	49	35	[17]
Rb	7	31	62	[124]
Cs	6	35	59	[124]
R_2Mg—RMgI *	28—32	45—49	23—25	[114]
R_2Ca—RCaI **	18—39	48—72	7—13	[95]
$CaZnR_4$	13	77	10	[12]
$Ca(AlR_4)_2$	15	80	5	[61]
R_2Sr **	27	64	9	[34]
$SrZnR_4$	20	70	10	[12]
Ba	75—80	9—13	11	[10]
R_2Ba	60—70	20—30	10	[32]
$BaZnR_4$ ***	18	76	6	[61]
$Ba(AlR_4)_2$	8	91	1	[61]
$Ba(OR)_2$+RLi	15—30	60—80	5—10	[86, 90, 125]
$Ba(OR)_2$+R_2Mg	15—30	60—80	5—10	[86, 90, 125]
oxolan				
RLi	7	7	86	[126]
RNa	5	16	79	[126]
RK, RCs	6—8	30—51	61—64	[126]
Mg	6****	39****	55****	[23]
R_2Ca—RCaI	12	17	71	[95]
R_2Sr	16	47	37	[34]
R_2Ba	28	50	22	[10]
hexamethylphosphorotriamide				
Li, Na, K	2—4	19—22	74—77	[109]
R_2Mg	4	16	80	[127]
Mg, Ca, Ba	4—7	19—22	74—77	[109]

*Temperature 90—100 °C.
**Initiator obtained in oxolan or ether with subsequent removal of solvent by distillation.
***Concentration of initiator ~3 mM.
****Oligomer.

The stronger coordinating power of alkaline-earth than of alkali metals is undoubtedly due to the presence of the double charge on the gegenions and hence to their increased acceptability for similar ionic radii. However, the enhanced ability of barium to form *cis*-1,4-polybutadiene, though noted some time ago[10,22] (and its ability to form isotactic poly(methyl methacrylate) was noted still earlier[120]), has not yet been rigorously explained.

Several publications (mainly patents) have recently appeared on the formation of polybutadiene in which the *trans*-1,4-structure predominates[86,89–91,125], under the influence of various initiators containing alkoxides or other oxygen-containing compounds of barium and alkyl derivatives of lithium or magnesium, between which exchange reactions undoubtedly occur. Since both lithium compounds and fully substituted barium alkyls are *cis*-regulating initiators for the polymerisation of butadiene, it is highly probable that unsymmetrical barium compounds of the type RBaOR′ are responsible for appearance of the *trans*-1,4-structure[86,87]. Investigation of such unsymmetrical compounds is of considerable general interest, since the possibility of introducing modifying groups directly into an active centre, which opens up wide prospects for controlling its catalytic properties, is evidently the most important fundamental feature of the systems that is absent in the case of univalent gegenions.

Table 2. Structure of isoprene polymers formed at room temperature by using initiators based on metals in Groups I and II.

Initiator	Content of monomer units, %				Ref.
	cis-1,4	*trans*-1,4	3,4	1,2	
hydrocarbon medium					
RLi	84—96	0—15	5—9	0	[131]
Na	0—4	12—46	51—77	6—11	[131]
K, Rb, Cs	0—20	40—55	32—40	7—9	[131]
R_2Mg—RMgI *	—	—	>95	—	[113]
Ca	72	0	28	0	[132]
R_2Ca—RCaI **	56	23	21	0	[7]
$CaZnR_4$ ***	12	73	15	0	[132]
Sr	46—56	0—12	35—44	0	[99, 103, 105]
R_2Sr **	38	24	37	1	[34]
$SrZnR_4$ ***	32	56	11	0	[132]
Ba	23—71	0—56	20—30	0	[99, 103, 105]
R_2Ba **	56	7	37	0	[133]
$BaZnR_4$ ***	34	53	12	0	[132]
oxolan					
RLi	0	0	74	26	[134]
R_2Ca—RCaI ****	0	69	31	0	[7]
Sr	53	12	27	8	[103]
R_2Sr	23	22	51	4	[34]
Ba	44	24	20	11	[103]
hexamethylphosphorotriamide					
RLi	0	4	58	38	[127]
R_2Mg	0	8	57	35	[127]
R_2Ca	0	0	55	45	[135]

*Temperature 90 °C.
**Initiator obtained in oxolan or ether with subsequent removal of solvent by distillation.
***Concentration of initiator ~3 mM.
****Polymerisation in diethyl ether.

Structural data on polyisoprene (Table 2) give no clear picture owing to their great scatter, at least partly due to the complexity of analysing the structure of this polymer. Alkaline-earth metals vary little in stereospecificity towards the polymerisation of isoprene. Comparison of corresponding metals in Groups I and II definitely reveals considerably higher contents of *cis*-1,4-units for the latter, although, in contrast to the polymerisation of butadiene, none of the alkaline-earth metals reaches the high level of stereospecificity characteristic of lithium compounds.

Influence of electron donors. Increase in the atomic weight of the metal whether in Group I or II produces a regular decrease in the proportion of 1,2-units when butadiene is polymerised in oxolan (Table 1), which is fully consistent with the corresponding decrease in the tendency of the cations to undergo solvation[17,136]. Even in this case, however, heavy alkaline-earth metals (strontium and barium) differ from their neighbours in Group I in a sharp increase in the content of 1,4-units. From solvents of ethereal type only strongly solvating multidentate agents (1,1-dimethylethylene, 3,6,9-trioxaundecane) give on polymerisation with a barium gegenion

the predominance of 1,2-units characteristic of anionic polymerisation[10,32,129]. In the highly polar hexamethylphosphorotriamide all metals in Groups I and II give polymers of almost the same structure. In general the structure of polyisoprene obeys the same laws; in any case there is a clear tendency for a greater proportion of 1,4-units with alkaline-earth metals when polymerisation occurs in oxolan.

The slight tendency of alkaline-earth metal cations to be solvated is well supported by other investigations. Thus in the polymerisation of butadiene with bistetraphenylbutylbarium introduction of oxolan up to a fiftyfold excess with respect to barium has hardly any effect on the structure of the polymer[98]; with larger quantities of oxolan a gradual transition of *cis*- into *trans*-1,4-units begins, but change in the proportion of 1,2-units is observed only when the oxolan content of the solution exceeds 10 vol.%.[32,129] With lithium initiators, on the other hand, a sharp increase in the proportion of 1,2-units has already begun with equimolecular proportions of oxolan and lithium[137], and in the presence of 1 vol.% of oxolan the resulting polymer has almost the same structure as in pure oxolan[17].

Polymerisation by dimetal complexes. Mixed compounds with zinc or aluminium alkyls form butadiene and isoprene polymers in which *trans*-1,4-structures predominate, independently of the nature of the alkaline-earth metal (Tables 1 and 2). Barium–aluminium complexes are distinguished by especially high stereospecificity: with respect to the total content of 1,4-butadiene units they are comparable with the most stereospecific catalysts based on transition metals. Barium–zinc alkyls are comparable with other organobarium initiators according to the overall rate of polymerisation[61,97]. The activity of barium–aluminium initiators is low[61], but the French Michelin firm has recently proposed in a series of patents several methods for enhancing their activity (with hardly any loss of stereospecificity)—by introducing electron donors[138], lithium alkoxides[139], or lithium alkyls[140].

Table 1 clearly reveals considerable structural differences between polybutadienes formed on compounds of alkaline-earth metals and on dimetal complexes, which are especially large with barium; hence the whole of the complex is directly involved in formation of the growing chain. In this respect alkaline-earth metals differ significantly from alkali metals, for which it has definitely been established that the introduction of diethylzinc or triethylaluminium affects only the overall rate of polymerisation, not the structure of the polymers (it is assumed that in this case complexes of the type $LiZnR_3$ or $LiAlR_4$ are inactive, while polymerisation occurs only on the uncomplexed portion of the initiator[2,61,132,141,142]). Thus systems based on alkaline-earth metals are sensitive not only to electron-donor agents but also to electron acceptors. This opens up new possibilities for controlling the stereospecificity of anionic initiators that are unknown for alkali metals.

Processes initiated by metal–zinc alkyls are characterised by an appreciable dependence of polymer structure on initiator concentration. Lowering the concentration of a barium–zinc alkyl from 3–5 m*N* to 0.1 m*N* increases the content of *cis*-1,4-butadiene units from 18–21% to 55–60% with a corresponding decrease in the proportion of *trans*-1,4-units (the 1,2-structure being constant), which is due to dissociation of the complex with separation of the free barium alkyl[61]. On the other hand, the polymerisation of isoprene by means of alkylzinc complexes of calcium, strontium, and barium in benzene (though in a different concentration range, 100–1 mM) exhibited the opposite relation: decrease in initiator concentration was accompanied by transition of *cis*- into *trans*-1,4-units[132].

(b) Acrylic monomers

Considerably less attention has been paid to this group of monomers than to dienes. Tetra-alkyls of zinc with calcium, strontium, and barium cause the formation of crystalline polymers of isotactic structure from iso-, s-, and t-butyl acrylates and methacrylates in toluene or ether[59]. In the polymerisation of methyl methacrylate in toluene, as in that of dienes, the variation in the stereoregulating action differs with metals in Groups I and II: the highest contents of isotactic structure are observed with the lightest alkali metal (lithium, up to 80%[143]) and with the heaviest alkaline-earth metal (barium 71%[120]). In oxolan, polymers having a predominantly syndiotactic structure are formed with all alkaline-earth metals[120].

Polymers of methyl methacrylate obtained by the action of dispersions of alkaline-earth metals in the presence of styrene (which does not enter the polymer chain) are enriched with the isotactic structure compared with those formed from the pure monomer[106]. Thus polymerisation by means of calcium in toluene increases the content of the iso-triad from 42% to 67%. It is assumed[106] that the structure of the polymer obtained in the presence of styrene characterises the actual anionic process, whereas in its absence the polymer is enriched with the syndiotactic structure owing to partial superposition of a radical process (another possible explanation will be given in Section IV).

Table 3. Composition of copolymers and copolymerisation constants r_1, r_2 in the presence of alkaline-earth metals.

Monomers		Initiator	Medium	M', mole %, in		r_1	r_2	Ref.
M	M'			initial mixture	copolymer			
Butadiene	styrene	RLi	benzene	50	9	12.5	0.1	[17]
Butadiene	styrene	Ca	toluene	—	—	6.7	0.01	[107]
Butadiene	styrene	RCaI	benzene	—	—	10	0.04	[95]
Butadiene	styrene	$CaZnR_4$	toluene	30	5	—	—	[12]
Butadiene	styrene	Sr	toluene	—	—	3.4	0.12	[107]
Butadiene	styrene	$SrZnR_4$	toluene	30	8	—	—	[12]
Butadiene	styrene	BaR_2	toluene	—	—	1.6	0.4	[107]
Butadiene	styrene	$BaZnR_4$	benzene	25	23	1.1	0.8	[96]
Butadiene	styrene	$ZaBnR_4$	benzene	30	22	1.3	0.7	[145]
Butadiene	styrene	$Ba(AlR_4)_2$	benzene	45	18	—	—	[145]
Butadiene	styrene	RLi	oxolan	50	85	0.2	8.0	[17]
Butadiene	styrene	RCaI	oxolan	—	—	0.6	1.7	[95]
Butadiene	styrene	BaR_2	oxolan	50	86	0.13	8.5	[96]
Butadiene	isoprene	RLi	toluene	50	29.5	—	—	[17]
Butadiene	isoprene	Ca	toluene	—	—	3.5	0.14	[107]
Butadiene	isoprene	Sr	toluene	—	—	4.3	0.3	[107]
Butadiene	isoprene	Ba	toluene	—	—	3.6	0.25	[107]
Butadiene	isoprene	BaR_2	benzene	50	31	2.0	0.3	[133]
Butadiene	isoprene	BaR_2	oxolan	50	20	3.0	0.1	[133]
Isoprene	styrene	RLi	toluene	50	12	9.5	0.25	[17]
Isoprene	styrene	Ca	toluene	—	—	4.5	0.07	[107]
Isoprene	styrene	RCaI	benzene	—	—	7.6	0.14	[95]
Isoprene	styrene	RCaI	oxolan	—	—	0.08	12	[95]
Isoprene	styrene	Sr	toluene	—	—	1.2	0.4	[107]
Isoprene	styrene	Ba	toluene	—	—	0.4	2.6	[107]
Butadiene	α-methylstyrene	BaR_2	benzene	56	0	—	—	[133]
Butadiene	α-methylstyrene	BaR_2	oxolan	54	10	—	—	[133]
Styrene	methyl methacrylate	BaR_2	benzene	50	100	—	—	[108]
Styrene	methyl methacrylate	BaR_2	oxolan	50	100	—	—	[108]

3. Copolymerisation

(a) Composition of copolymers

The copolymerisation of butadiene with styrene has been the most intensely studied, since copolymers having a random distribution of monomer units in the polymer chain provide

one of the main forms of high-volume general-purpose synthetic rubbers, and great interest has recently arisen in the search for catalysts ensuring the production of these rubbers under industrial conditions of solution polymerisation[6].

Table 3 shows that in oxolan, as with alkali metals, styrene is a considerably more reactive monomer than is butadiene. In the presence of initiators based on calcium and strontium in a hydrocarbon medium, as with lithium compounds, the copolymers are considerably enriched in butadiene. Yet butadiene–styrene copolymerisation constants are closely similar in most barium systems. It is interesting that this property is maintained in such structurally different compounds as barium alkyls and barium–zinc tetra-alkyls, despite the difference in their stereoregulating action. It is significant that the resulting copolymers contain considerably fewer 1,2-units than in radical polymerisation (10% on BaR_2 and 5% on $BaZnR_4$ compared with 20% in a radical polymer[6]) and are unlike modified lithium systems[144] in not containing microblocks.

Thus barium compounds are the only individual type effecting the formation of butadiene–styrene copolymers having a random distribution of monomer units in the chain with a low content of vinyl groups (sodium initiators also give similar copolymerisation constants, but with a content of vinyl groups exceeding 30% [17]). Depending on the type of initiator, copolymers can be obtained containing predominantly either *cis*-1,4-units (barium alkyls) or *trans*-1,4-units (barium–zinc alkyls or barium–aluminium alkyls with modifying additives). According to information in the patent literature both types of copolymers are suitable as rubbers.

Other copolymerisation systems have been investigated less thoroughly, and differences in behaviour between alkaline-earth and alkali metals are not so substantial (Table 3). Copolymerisation of styrene with methyl methacrylate on an organobarium initiator has confirmed that a homopolymer of the latter monomer is actually formed under homogeneous conditions, although with heterogeneous initiation by dispersions of alkaline-earth metals a certain quantity of styrene enters the copolymer[11,122] (the reasons for this have been discussed in detail above).

Thus in oxolan the relative reactivities of the monomers increase in the sequence

α-methylstyrene ≪ isoprene < butadiene < styrene ≪ methyl methacrylate

characteristic of anionic polymerisation. On calcium and strontium initiators in a hydrocarbon medium the activity varies in the sequence

styrene < isoprene < butadiene

as with lithium. A somewhat different dependence is observed on a barium initiator:

α-methylstyrene ≪ isoprene < butadiene ≅ styrene ≪ methyl methacrylate

(b) Structure of copolymers

It is usually supposed (explicitly or implicitly) that in anionic copolymerisation, as in the radical process, the presence of the second monomer M′ does not affect the addition of the monomer unit M, i.e. that the structure of M units is the same in the copolymer as in the homopolymer obtained under the same conditions. Only recently has it appeared that styrene influences the structure of diene units in copolymers formed by the action of lithium initiators[146,147]. However, the interaction of monomers in anionic processes has been most fully investigated on barium initiators, where it is apparently general in character (for coordination polymerisation involving transition metals this phenomenon was known considerably earlier[148]).

Table 4. Structure of butadiene part of copolymer with styrene obtained by using bis-1,1,4,4-tetraphenylbutylbarium[96,133].

Styrene in copolymer, mole %	Monomer units, %			Styrene in copolymer, mole %	Monomer units, %	
	cis-1,4	*trans*-1,4	1,2		1,2	1,4
	benzene				oxolan	
0	63	25	12	0	22	78
14	62	27	11	16	26	74
20	57	29	14	34	49	51
25	52	34	14	47	45	55
37	50	40	10	66	51	49
45	36	54	10	84	51	49
69	34	54	12	93	61	39

In the copolymerisation of butadiene with styrene by means of bistetraphenylbutylbarium in benzene (Table 4) increase in the styrene content of the copolymer is accompanied by a gradual conversion of *cis*- into *trans*-1,4-units while the content of 1,2-units remains unchanged (a high content of the *cis*-1,4-structure is maintained in the composition range of practical interest for the production of rubbers, i.e. at styrene contents up to 15 mole %). In oxolan the introduction of styrene produces a sharp increase in the content of 1,2-units (Table 4). Similarly, increase in the content of butadiene in its copolymer with isoprene (polymerisation in benzene) is accompanied by increase in the content of *trans*-1,4-units (up to 43% at a butadiene content of 69 mole %) with a corresponding decrease in the proportion of *cis*-1,4-units, the structure of the butadiene portion changing little[133]. Thus according to their influence on the structure of the diene units these monomers can be arranged in the sequence isoprene < butadiene < styrene, in which each successive member affects the structure of the preceding member, bringing it closer to that characteristic of systems with alkali metals[133].

Discussion of possible reasons for this phenomenon[32,133] shows that solvation of the gegenion by the second monomer M′ plays no decisive part. It is supposed that the main factor in copolymerisation in benzene is the decrease, with increased polarity of the bond with the terminal monomer unit in the above sequence, in the ability of the gegenion to *cis*-orient the monomer unit that is added on. (It is noteworthy that, in copolymerisation by means of a *trans*-orienting organobarium–zinc initiator, the structure of the butadiene units corresponds to that of the homopolymer throughout the composition range[145].) Thus in this process entry of M′ into the chain apparently changes the structure of the following M unit. When copolymerisation occurs in oxolan, introduction of M′ probably changes the structure of the preceding M unit (styrene adds with equal probability to α- and γ-carbon atoms of a terminal allyl unit, whereas butadiene adds predominantly to the α-atom[133]).

Thus the main features of alkaline-earth metals are higher coordinating power, lower sensitivity to electron donors, sensitivity to organometallic electron-accepting complexing agents, and the possibility of introducing modifying groups directly into the gegenion. The last two factors extend significantly the possibilities for controlling the catalytic

activity of these compounds, in definite measure assimilating them to systems based on transition metals. It is sufficient to state that barium initiators represent the first (and only) case in anionic polymerisation in which it is possible to obtain on the same metal butadiene polymers in which any of the possible structures predominates—*cis*-1,4 (BaR_2 in a hydrocarbon medium), *trans*-1,4- (barium–aluminium or barium alkoxide systems), or 1,2-structures (BaR_2 in the presence of 1,1-dimethylethylene or hexamethylphosphorotriamide).

In regard to immediate prospects for practical application a leading position is occupied without doubt by organobarium initiators for the copolymerisation of butadiene with styrene. There are grounds for supposing that, with respect both to the properties of the resulting rubbers and to the general characteristics of the industrial process, barium initiators are fully compatible with lithium initiators, while still inferior to them in economy and simplicity of production.

According to the Phillips Petroleum Col. partly crystalline *trans*-1,4-polybutadiene formed by means of barium alkoxide initiators is also an interesting material with valuable new technical properties[149].

IV. KINETICS AND MECHANISM OF POLYMERISATION IN SYSTEMS WITH BIVALENT GEGENIONS

1. Structure of Active Centres—Physicochemical Investigations

A most characteristic feature of anionic polymerisation is the existence of active centres in diverse forms—molecules having a polarised bond, their association complexes, ion-pairs varying in degree of solvation, free ions, ion-triplets, etc.—differing in their reactivity and stereospecificity[17-19]. (As a distinction from free ions the remaining forms of active centres are sometimes described in general as "combined with a gegenion".) This is fully applicable also to alkaline-earth metals, with which, however, certain complications in terminology arise (thus an electrically neutral species of type (R^-, M^{2+}, R^-) must obviously be termed an ion-pair, although it contains three ions, while the charged species (R_3^{3-}, M^{2+}) is a triplet, etc.). Furthermore, novel forms of active centres appear, that are non-existent or not specially significant in processes with alkali metals.

We must first note the peculiar structure of live polymers having carbanions at both ends of the macromolecule. Early papers on the preparation of a double-ended initiator, bis-tetraphenylbutylbarium[10,26], had already mentioned that from stoichiometric considerations this compound could not exist in a linear monomeric form. Subsequent investigation by various physicochemical methods of this initiator and the double-ended live polymers of styrene and butadiene formed in its presence showed[31,32] that in electron-donor solvents (oxoland, dimethyl ether) these compounds form macrocyclic aggregates, whose presence is responsible for several anomalies in the properties of the systems and also several peculiarities in the polymerisation processes occurring in them. In particular the electrical conductivity of the systems is significantly smaller than that of their single-ended analogues, since the primary dissociation products of macrocycles are non-conducting zwitterions, while the variation of the conductivity with concentration does not correspond to Ostwald's dilution law for weak electrolytes.

It is important to emphasise that, in contrast to other cases of the association of active centres (e.g. lithium compounds in a hydrocarbon medium), in which entry into the association complex changes significantly the character of the metal–carbon bond, in the present case the union of several species to form a single aggregate produces no appreciable change in the nature of the individual active centres in comparison with their single-ended analogues. Formation of similar cyclic aggregates has been established also for products of the action of magnesium on 2-vinylpyridine[150] and on isoprene in oxolan[118]. The latter work has confirmed the previously observed[31,32] decrease in number of fragments in the ring with increase in the length and hence flexibility of individual fragments.

A novel form of active centres, not present in alkali-metal systems, is provided also by "unsymmetrical" ion-pairs, i.e. species of the type (R^-, M^{2+}, R^{2-}), which play an important part in several processes, but as yet have hardly been studied by physicochemical methods.

Table 5. Wavelengths λ_{max} (nm) in absorption spectra of model compounds $R.C(C_6H_5)_2^-M^+$.

Cation	Solvent		Ref.
	benzene	oxolan	
Lithium	420	490	[151]
Sodium	460	480	[151, 153]
Magnesium	—	<330; 490*	[154]
Magnesium	—	298**	[155]
Calcium	460	520	[154]
Strontium	470	470	[154]
Strontium	—	465	[35]
Barium	445	445	[154]
Barium	—	448	[33]

*Below −60 °C.
**Diphenylmethylmagnesium bromide in diethyl ether.

One of the main factors determining the reactivity and the stereospecificity of active centres is the degree of polarisation of the bond between the growing end of the chain and the gegenion. If is often estimated from the electronic absorption spectra of model compounds containing carbanions of the 1,1-diphenylalkyl type[17,151,152]. Spectral data (Table 5) together with results on the structure of butadiene polymers (Table 1) show that the correlation between λ_{max} and the character of polymerisation (the shorter the wavelength λ_{max}, i.e. the less polar the bond, the greater the proportion of the coordination process leading in particular to increase in the content of 1,4-diene structures), established for alkali-metals[17,136], is maintained for alkaline-earth metals.

According to the λ_{max} wavelength in oxolan the polarity of the metal–carbon bond in the series of alkaline-earth metals (apart from magnesium, which is inactive in polymerisation), as in the series of alkali metals[17,136], decreases as the ionic radius increases, with a corresponding diminution in the proportion of 1,2-units in the butadiene polymers, which is well explained by the weakening role of solvation effects in the same sequence. For a 1,1-diphenylalkylbarium in oxolan λ_{max} lies ar appreciably shorter wavelengths compared not only with other compounds in the same solvent but even with the diphenylalkylsodium in benzene. Hence a polybutadiene obtained by the action of barium compounds in oxolan contains more 1,4-units than do polymers obtained with alkali metals (other than lithium) in a hydrocarbon medium. This indicates unusually low polarity of the bond in a barium active centre.

In a hydrocarbon medium alkali and alkaline-earth metals show opposite variations: whereas among the alkali metals the polarity of the metal–carbon bond increases with the ionic radius of the metal, the polarity diminishes on passing from calcium to barium (the λ_{max} given in Table 5 for a 1,1-diphenylalkylstrontium in benzene may be too high[154] owing to incomplete removal of the oxolan used in the preparation). A possible explanation of such divergence is the early view[17] that the polarity of a metal–carbon bond (in a given carbanion) should increase with decrease in the electron-accepting properties of the metal. Calculation showed[156] that the electron affinity (a measure of electron-accepting properties) falls with increase in atomic number in the series of alkali metals, but increases in the alkaline-earth metals, owing to the difference in type of hybridisation of the lowest vacant orbitals—*s* in alkali metals and *sd* in alkaline-earth metals.

Table 6. Conductivity data for systems containing alkaline-earth metals in oxolan.

Metal	Temp., °C	K_{diss}, M	Ref.
	fluorenyl		
Sodium	20	$7.5\cdot10^{-7}$	[78]
Caesium	25	$1.4\cdot10^{-7}$	[157]
Strontium	20	$1.7\cdot10^{-7}$	[78]
Barium	20	$5.3\cdot10^{-9}$	[78]
	tetraphenylborate		
Sodium	25	$8.5\cdot10^{-5}$	[158]
Caesium	25	$1.87\cdot10^{-5}$	[158]
Barium	25	$3.6\cdot10^{-5}$	[31]
Barium	20	$1.65\cdot10^{-5}$	[159]
	triphenylmethyl		
Sodium	25	$7.6\cdot10^{-6}$	[160]
Barium	25	$3.6\cdot10^{-7}$	[31]
	benzyl (styryl)		
Sodium	25	$1.5\cdot10^{-7}$	[18]
Caesium	25	$2.8\cdot10^{-9}$	[18]
Barium	20	$1.1\cdot10^{-10}$	[159]
Barium	25	$4.1\cdot10^{-11}$	[161]

Valuable information on the state of active centres in solvating media is given also by conductivity measurements (Table 6). In ethereal solvents (oxolan, dimethyl ether) barium compounds at concentrations up to 10 μM undergo only the first stage of dissociation[31,32,69], without formation of free Ba^{2+} ions (the values of K_{diss} in Table 6 relate to this stage):

$$BaR_2 \overset{K_{diss}}{\rightleftarrows} [BaR]^+ + R^- \quad . \qquad (1)$$

Compounds containing a barium–carbon bond have considerably lower conductivities than those of alkali metals, in particular for the caesium analogue of the barium compound. This also indicates the low polarity of this bond.

2. Principal Kinetic Laws

The few kinetic investigations have already covered a fairly wide range of polymerisation systems. In most cases initiation stages are rapid, and termination reactions are absent. It is therefore supposed that, where not specially stipulated, the measured rate of polymerisation is the rate of chain growth, as in most research with alkali metals. Published kinetic data are summarised in Table 7.

First order of chain growth with respect to the monomer has been established in all cases without exception. Since the order of reaction with respect to the initiator differs in different systems, the reaction velocity is usually characterised by the experimental first-order rate constant

$$k' = -\frac{1}{M}\cdot\frac{dM}{dt},$$

where M is the concentration of the monomer. The growth constant k_{gr} cited in several papers is calculated: $k_{gr} = k'/c_0$, where c_0 is the concentration of growing chains. This constant acquires real meaning only when chain growth is first order with respect to active centres.

Table 7. Kinetic characteristics of chain growth in polymerisation by using compounds of alkaline-earth metals (not indicated over the concentration range of active centres c_0 = 1–10 mM).

Monomer	Initiator	Order with respect to indicator	T, °C	10^3c_0, mM	$10^3k'$, s^{-1}	k_{gr}, $M^{-1}s^{-1}$	E_{gr}, kJ mole^{-1}
		oxolan					
Styrene	dibenzylcalcium	0	−30	—	5.5	—	—
Styrene	dibenzylstrontium[166,175]	0	20	—	36	—	—
Styrene	dibenzylbarium[161]	0	30	—	1.0	0.33	35
Styrene	bistriphenylmethylbarium[163]	1	30	—	—	0.019	54
Butadiene	dibenzylstrontium[164]	1	30	—	—	$1.5\cdot10^{-3}$	56
Butadiene	dibenzylbarium[161]	1	30	—	—	$8\cdot10^{-3}$	57
Butadiene	bistriphenylmethylbarium[163]	1	30	—	—	$1\cdot10^{-2}$	56
2-Vinylpyridine	oligovinylpyridine magnesium*[150]	variable	20	0.04	2.8	70	
			20	0.06	2.7	45	
		$0<n<1$	20	0.24	5.5	23	
			20	0.9	10.8	12	
MMA	difluorenylbarium[165]	1	−70	—	—	11.5	20
		benzene					
Styrene	bistriphenylpropylbarium[97]	1	30	—	—	0.39	35
Butadiene	bistriphenylpropylbarium[97]	1/3	30	0.24	0.015	—	—
			30	12	0.083	—	67

*Difunctional initiator.

(a) Electron-donor media

Styrene. The most peculiar behaviour has been revealed in the polymerisation of styrene in oxolan. The most important feature is the existence of completely different kinetics for barium initiators of three different types.

The first type—a single-ended initiator with rapid initiation (dibenzylbarium)—has been studied simultaneously by two groups of investigators[69,159,161], who have obtained almost identical results. The measured rate of polymerisation (and hence the rate of chain growth) is independent of the concentration of active centres, so that the usual calculated quantity k_{gr} increases with dilution in inverse proportion to the initiator concentration. Such an unusual law could be explained[69,161] on the principal (established earlier for alkali metals[18]) that free carbanions play a decisive part in the anionic polymerisation of styrene, by introducing the hypothetical formation of more complicated species, "ion-triplets", by coordination of an additional styryl carbanion with the barium cation, which though weakly solvated has a

strong electrostatic field:

$$R^- + BaR_2 \overset{K_{tr}}{\rightleftarrows} [BaR_3]^- \quad (2)$$

On the postulates that equilibrium (2) is displaced to the right and that the total concentration of charged species is small (as follows from the low conductivity of the system—Table 6) calculation by means of Eqns.(1) and (2) yields the kinetic formula

$$k' = -\frac{1}{M}\cdot\frac{dM}{dt} = k_-\cdot c_- = k_-(K_{diss}/K_{tr})^{1/2} \quad (3)$$

consistent with experimental results (k_- is the growth rate constant on free anions and c_- the concentration of free styryl anions).

With the same postulates the suggested scheme predicts that the equivalent conductance of the system shall be independent of c_0. Such behaviour, which is also unusual for solutions of weak electrolytes and is due to the "asymmetry" of formation of the ion-triplets (as stated above, only the negative triplet of type BaR_3^- is formed, not the positive $Ba_2R_3^+$), has been confirmed experimentally for live barium–polystyrene[69] and for dibenzylbarium[161]). The combination of kinetic and conductivity data has permitted calculation of the dissociation constant K_{diss} (Table 6), which from the above discussion evidently cannot be obtained directly from conductivity measurements. (Ion-triplets are not formed in compounds of barium with branched carbanions such as di- and tri-phenylmethane, and the conductivity depends on the concentration[31].)

Recent preliminary reports indicate (Table 7) that this scheme is followed also by the polymerisation of styrene in oxolan under the influence of corresponding calcium and strontium initiators. The overall rate of polymerisation increases from barium through strontium to calcium (apparently owing to the accompanying increase in the dissociation constant K_{diss} and hence in the concentration of free ions[166]). This recalls the situation presented by the alkali metals, when the increase in rate of polymerisation of styrene accompanying each passage from a lower to a higher member is associated with successive increase in K_{diss}, not with change in reactivity of individual species[18].

An initiator of the second type—double-ended with rapid initiation—was historically the first organobarium subject (a barium salt of an oligomeric dianion of α-methylstyrene) of kinetic investigation[167]. Zero order with respect to the initiator was observed for the first time[167], but this was given an untenable explanation (formation of inactive association complexes of active centres), which has subsequently been criticised[69,70,150,161]. Only after the above results had been obtained for the simpler system with dibenzylbarium did it become clear that the zero order with respect to active centres has the same causes here as in the preceding case, i.e. formation of ion-triplets with free ions is kinetically decisive, and views developed subsequently by various authors[70,162] have in the main shown mutual agreement.

The most significant kinetic feature of the polymerisation of styrene with double-ended initiators, which is directly connected with the above formation of macrocyclic aggregates, is that the observed growth constant increases with length of the polymer chain, with consequent autocatalysis despite rapid completion of the initiation stage[10,161,163,168]. Thus at 20 °C the constant k' (in 10^{-3} s^{-1}) increases from 0.25 to 2.0 as the degree of polymerisation rises from 50 to 800.[162] During the polymerisation of styrene (and also of butadiene) in the presence of bistetraphenylbutylbarium the conductivity of the system increases steadily[31,32], which agrees well with the theoretically predicted increase in the constant for the dissociation of cyclic ion-pairs into free ions as the ring becomes larger[18,169]. In conformity with Eqn.(3) increase in K_{diss} leads to increase in the overall rate of polymerisation of styrene.

Only the number of growing chains in the macroring remains obscure. Viscosimetric data[31,32] show that a ring contains 5–7 polystyrene chains halfway through the process, and 3–4 chains at the end. On the other hand, closure of an intramolecular ring from one chain has been assumed, although a fall in viscosity on deactivation was also observed[162], corresponding to a mean degree of association of 1.5–4 (closure of a monomolecular ring should have led to an increase in viscosity). Apparently the most serious (and only) argument in support of a monomolecular ring is the same workers' observation[170] of non-random spontaneous deactivation of solutions of oligomeric styrylbarium dianions in oxolan on reaction with the solvent. Deactivation of one live end caused rapid deactivation of the other, which could be explained only if the two ends were attached to the same gegenion. We remark merely that actual formation of macrorings is sufficient, independently of their size, for the above interpretation of the dependence of rate of growth on chain length.

Finally, a third, completely different type of behaviour is observed on using the relatively inactive (single-ended) initiator bistriphenylmethylbarium[70,163], when the process is autocatalytic, as is usual for reactions having a slow initiation stage. The rate of chain growth (for a given concentration of growing chains) is less than one-tenth of the rate with dibenzylbarium (Table 7) and, most significantly, depends on the concentration of active centres. The non-zero reaction order is qualitatively evident from the very fact that the rate increases with number of growing chains. Mathematical treatment by several methods[70,163] has established that chain growth is first order with respect to active centres.

It is still more surprising that the resulting polymers have comparatively low molecular weight ($\bar{M}_n \cong 10000$ at 30 °C), lower by factors of 20–40 and more than the calculated value, and an extremely wide molecular-weight distribution ($\bar{M}_w/\bar{M}_n \cong 2$, whereas with live polymers slow initiation is able to raise this ratio to at most 1.3–1.4 [16]). Detailed analysis of the results indicated the occurrence of chain transfer to the monomer (probably by transfer of a hydride ion)[163]. This is perhaps the most unexpected fact, since hitherto the anionic polymerisation of styrene has been regarded as the most typical example of the formation of live polymers.

The distinguishing behavioural features of this system can be understood on the basis that, owing to the extremely low rate of initiation ($k_{in} = 2.2\times10^{-6}$ M^{-1} s^{-1} at 30 °C), most of the active centres have the structure of the unsymmetrical ion-pair ($C_6H_5.CH:CH-Ba-C(C_6H_5)_3$: i.e. they contain a triphenylmethyl group attached to the gegenion. Such active centres will dissociate preferentially at the considerably more polar $(C_6H_5)_3C-Ba$ bond (Table 6): dissociation at the $C_6H_5.CH:CH-Ba$ bond is suppressed by the presence of $[(C_6H_5)_3C-Ba]^+$ cations formed by dissociation of unchanged initiator $[(C_6H_5)_3C]_2Ba$, a strong electrolyte. As a consequence the content of $C_6H_5.CH:CH^-$ ions is much lower than in the previous cases, and the contribution by ion-pairs becomes predominant, which well explains both the general decrease in rate of chain growth and the appearance of first order with respect to active centres. Addition of styrene to a bulky active centre containing four phenyl groups around a cation apparently meets considerable difficulties, which greatly increase the probability of chain transfer but also influence significantly copolymerisation processes (for greater detail see below).

Thus in the polymerisation of styrene on barium initiators in oxolan the nature of the hydrocarbon moiety of the initiator has a significant influence on fundamental aspects of chain growth and on the nature of the resulting polymers.

Other monomers. The polymerisation of butadiene in oxolan under the influence of dibenzylbarium[161] and of dibenzylstrontium[164] is first order with respect to the initiator. Hence, as with alkali metals[171], the decisive role in steps of chain growth belongs not to free ions but to forms of active centres "combined with a gegenion". Together with the above data on the structure of the polymers and the spectra of model compounds this led to the conclusion that the active centres of chain growth in the polymerisation of butadiene by means of barium[161] and probably strontium[164] are molecules having a polarised metal–carbon bond. Live polymers of butadiene, formed under the influence of double-ended bistetraphenylbutylbarium, exhibit the same peculiarities of conductivity and viscosity behaviour, associated with the formation of macrocyclic aggregates, as do styrene systems[31]. Since free ions have no decisive role in the polymerisation of butadiene, it is clear that variation in the dissociation constant does not affect the kinetics[161]. When polymerisation occurs under the influence of bistriphenylmethylbarium an induction period is observed, as in the case of styrene, that is due to slow initiation ($k_{in} = 1.1 \times 10^{-5}$ M^{-1} s^{-1} at 30 °C)[163]. Chain growth is first order with respect to active centres, with growth constants closely similar to those obtained with dibenzylbarium (Table 7). Hence butadiene adds at about the same rate to the two types of active centres—"symmetrical" ($CH_2:CH.CH:CH-Ba-CH:CH.CH:CH_2$) and "unsymmetrical" [$CH_2:CH.CH:CH-Ba-C(C_6H_5)_3$].

Comparison of published data shows that the rate of polymerisation of butadiene in oxolan is greatest with barium, the highest alkaline-earth metal[161]; the process is slower with strontium[164], and perhaps still slower with calcium[95]. This corresponds with the variation found with alkali metals[126], but the overall rates are considerably lower than with the latter.

A pattern similar to that with butadiene is observed[165] in the polymerisation of methyl methacrylate in oxolan by means of a barium compound at −70 °C (under these conditions a live polymer is formed; at higher temperatures intramolecular chain termination takes place with involvement of ether side-groups). The reaction is first order with respect to the initiator on both single- and double-ended initiators (difluorenyl- and bistetraphenylbutyl-barium), and occurs at the same rate. Hence, as in the polymerisation of butadiene, it takes place on "combined with a gegenion" active centres (in the present case on ion-pairs[165]).

A more complicated dependence is obtained in the polymerisation of 2-vinylpyridine under the influence of a double-ended magnesium initiator[150]. The concentration dependence of the observed chain-growth constant is described by an equation of the type $k_{gr} = a + bc_0^{-1}$ (or $k' = ac_0 + b$). The same scheme is adopted as for the polymerisation of styrene with dibenzylbarium (allowing for the formation of ion-triplets), but in this case not only free ions but other species (ion-pairs or -triplets) take part in chain growth, their contribution to the total rate of polymerisation being proportional to the initiator concentration. Viscosimetric data indicate the formation of macrocyclic aggregates in the double-ended system, but polymerisation occurs[150] without autocatalysis. Unfortunately the kinetics of polymerisation with a single-ended initiator was not examined[150].

It is interesting that, when a relatively inactive initiator (dibenzylmagnesium) is used, spectral and viscosimetric data indicate formation of unsymmetrical active centres of type $NC_5H_4.CH:CH.Mg.CH_2.C_6H_5$, which differ in properties from $NC_5H_4.CH:CH.Mg.CH:CH.C_5H_4N$ centres[150].

(b) Hydrocarbon medium

The kinetics of the polymerisation of butadiene and styrene in benzene have been investigated[97] in the presence of bis-1,1,3-triphenylpropylbarium, which had been obtained in oxolan and then distilled with chromatographic control of completeness of removal. The order of chain growth with respect to the initiator concentration in the polymerisation of butadiene is close to one-third, which indicates the association of active centres usual in anionic polymerisation in hydrocarbon media, in this case formation of trimeric complexes. The polymerisation of styrene, on the other hand, is first order with respect to the initiator, and hence polystyrylbarium active centres are unassociated even in benzene. Association of polybutadienylbarium active centres and non-association of polystyrylbarium have been confirmed by viscosimetric data[97]. In the polymerisation of butadiene in benzene by means of double-ended bistetraphenylbutylbarium, when association should lead to the formation of a kind of three-dimensional network, "gelation" of the solution was already observed at low degrees of conversion of the monomer, but the solution again became mobile on deactivation[129].

According to the above results styrene is polymerised more rapidly than butadiene by barium compounds in benzene. In the presence of a mixed calcium initiator $R_2Ca-RCaI$, on the other hand, rates of homopolymerisation correspond to the sequence butadiene > isoprene > styrene[95] (the rates of polymerisation of both butadiene and styrene were lower here than with a barium initiator). The activation energy of the polymerisation of butadiene by means of this initiator is 87 kJ $mole^{-1}$.[8]

Overall rates of polymerisation of butadiene and styrene by means of barium compounds in benzene are closely similar to rates observed with lithium initiators[172]. Since, however, both polystyryl- and probably also polybutadienyl-lithium active centres are considerably more strongly associated than are barium centres, the relatively high rate of polymerisation on barium initiators is clearly due to a greater effective concentration of active centres, not to their reactivity.

One of the most characteristic features of anionic polymerisation with alkali metals is the sharp increase in its overall rate on passing from hydrocarbon to electron-donor solvents. With barium initiators, however, Table 7 shows that over the usual concentration range (10–1 mN) transfer from benzene to oxolan produces no appreciable increase in total rate of polymerisation. Since in the polymerisation of butadiene in benzene chain growth involves only a small fraction of unassociated active centres, whereas polymerisation of styrene in oxolan occurs predominantly on free ions with an insignificant contribution by ion-pairs, it is obvious that the reactivity of "combined with a gegenion" forms of polybutadienyl- and polystyryl-barium active centres is higher in benzene than in oxolan[97]. In the polymerisation of styrene under the influence of "butylcalcium iodide"[95], on the other hand, transfer from benzene to oxolan causes a sharp increase in total rate (by several orders of magnitude), as with alkali metals.

3. Mechanism of Copolymerisation

The influence of the hydrocarbon part of the initiator on the character of the processes initiated, which is specific to

alkaline-earth metals and has been reported in the preceding subsection, is just as clearly evident in copolymerisation. The main features of the copolymerisation of butadiene with styrene by means of bistriphenylmethylbarium in oxolan differ significantly[173] from those of copolymerisation initiated by other barium compounds (Section III). Whereas with dibenzylbarium styrene is considerably more active than butadiene (Table 3), in the presence of the former initiator the activities of the monomers level out ($r_1 = r_2 = 1.0$).

Estimation of the rates of indibidual primary steps (by comparing copolymerisation constants with homopolymerisation rate constants of the same monomers) showed that in the presence of bistriphenylmethylbarium the rates of both styrene-addition steps (to its own and to a butadiene active centre) fall by more than 90%, whereas the rates of addition of butadiene to both growing chains remain almost unchanged[173] (this work[173] was done before it became clear that transfer from one initiator to another causes a complete change in the mechanism of individual primary steps; this result can therefore be regarded merely as a qualitative indication of an appreciable decrease in reactivity of styrene as a consequence of the presence of a triphenylmethyl group in the active centre). Such presence influences also the structure of the copolymers[173]. Whereas in copolymerisation by means of "ordinary" barium initiators increase in the styrene content is accompanied by enrichment of the butadiene part with 1,2-units (Table 6), in the presence of bistriphenylmethylbarium introduction of up to 60% of styrene into the copolymer does not affect the structure of the butadiene units. (All the above applies to copolymers obtained in the initial stages: with high conversions, when "symmetrical" active centres begin to appear, a non-uniform copolymer is formed, enriched with styrene and 1,2-butadiene units[173].)

Effects due to interaction of groups in an active centre may obviously be still more widely evident in copolymerisation than in homopolymerisation, since growing chains with different kinds of terminal units can here act as "perturbing" groups. Interpretation of the results is, of course, considerably complicated thereby, but a broad field is opened up for research. Thus investigation of the influence of styrene on the structure of butadiene units in copolymers formed under the influence of barium compounds has revealed[32,96,133] that calculations based on simple models regarding growing chains as isolated will not give a quantitative description of the results. Thus the structure of the resulting monomer unit obviously depends not only on the structure of "its" growing chain but also on the nature of the terminal unit of the adjacent chain combined with the same gegenion.

Results obtained[106] on the structure of poly(methyl methacrylate) formed in the presence of styrene are relevant here. The explanation given (a competing radical process) is open to doubt (Section III). An alternative explanation of this effect may be that, as mentioned earlier, styrene is preferentially involved in initiation when a mixture with methyl methacrylate is in contact with a heterogeneous initiator[18,123], so that subsequent polymerisation of the methacrylate takes place on "unsymmetrical" centres of the type $C_6H_5.CH:CH-Ca-CH:C(CH_3).COOCH_3$.

Such effects due to interaction between two different groups attached to the same gegenion undoubtedly play an important part in homo- and co-polymerisation initiated by compounds of alkaline-earth metals (as also in the chemistry of these compounds in general). Unfortunately the almost complete absence of quantitative experimental data does not permit even qualitative prediction of the direction of this influence. As yet only the single observation can be cited[159] that the dissociation constant of the unsymmetrical styrene–phenylborate salt $C_6H_5.CH:CH.Ba.B(C_6H_5)_4 \rightleftharpoons [C_6H_5.CH:CH.Ba]^+ + B(C_6H_5)_4^-$ in oxolan is roughly double that of symmetrical barium tetraphenylborate. Thus in this case introduction of a less polar group (styryl) causes additional polarisation of the bond with the more polar group.

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The results discussed above confirm the validity and usefulness of many fundamental principles of the theory of anionic polymerisation developed for alkali metals, but also reveal several fundamentally novel forms of behaviour not observed previously. The behavioural features of alkaline-earth metals can be divided (more or less arbitrarily) into two groups. Such phenomena as the presence of unsymmetrical active centres or the formation of live macrorings in double-ended systems are due to the actual bivalency of the gegenion; they should, of course, occur to some extent in processes with all Group II metals. Other phenomena—e.g. low polarity of the metal–carbon bond, enhanced coordinating power in the polymerisation of butadiene, low sensitivity to electron donors, less tendency to association in a hydrocarbon medium, etc.—are connected mainly with the specific electronic structure of actual gegenions, and are usually most strongly developed with the heavier metals (barium and strontium).

Discovery and investigation of all these novel phenomena will both broaden significantly our general theoretical ideas on anionic polymerisation and open up new prospects for their practical application. Although possible uses of alkaline-earth metals in polymerisation are more or less determined (conclusion to Section III), at least for the immediate future, theoretical aspects of this field are only beginning to be worked out. There is every reason to expect that further research will not only prove fruitful in developing the new field—polymerisation by means of alkaline-earth metals—but will also help to shed new light on many phenomena in the "old" field (polymerisation on alkali metals), as has already been observed more than once in the theory of anionic polymerisation, with expansion of the range of materials investigated.

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Electron Transfer in Photochemical Reactions

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Modern ideas concerning the mechanism of electron transfer in photochemical reactions in solution are discussed. The quenching of the excited state via the electron transfer mechanism, the intermediate states and the role of the medium in the formation of radical-ions, the reactivity of excited states in the electron transfer reaction, and the energetics of this reaction are examined.
The bibliography includes 203 references.

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I. INTRODUCTION

Among different types of photochemical reactions, the electron transfer process is one of the most common. Electron transfer processes constitute the basis of many reactions in organic photochemistry (for example, heterolytic substitution reactions[1-4]) and the photochemistry of coordination compounds[5-8], the photochemical methods for recording information[9,10] and in the first place spectral sensitisation in photography[11-14], the photodegradation of dyes[15], and many photobiological processes, for example, photosynthesis[16,17]. Photochemical oxidation-reduction reactions with participation of aromatic, carbonyl, and heterocyclic compounds[4,18], dyes of different classes[15,19-21], pigments[22-25], and coordination compounds[5-8], and inorganic ions[26-28] are widely investigated.

Definite advances, due primarily to progress in the development of experimental technique, have been achieved in recent years in this field of photochemical reactions. The application of nano- and pico-second lasers made it possible to investigate in detail the mechanism of electron transfer and the properties of the intermediates of oxidation-reduction photoreactions. Numerous studies, whose aim was to establish a correlation between the efficiency of the electron transfer and the properties of the reacting molecules and also studies devoted to the investigation of the energetics and kinetics of the electron transfer reaction, the elucidation of the role of the medium, etc. have been published recently.

This review deals with the current ideas about the mechanisms of electron transfer in photochemical reactions in solutions. Modern views on the mechanism of oxidation-reduction photoreactions are to some extent based on the

available theories of electron transfer[29-32] and also on the characteristic features of the behaviour of excited molecules.

II. ENERGETICS OF THE ELECTRON TRANSFER REACTION

Photochemical reactions (including electron transfer reactions) begin with the absorption of light by the molecular system, which leads to the formation of electronically excited states. The properties of molecules in the excited state can differ from their properties in the ground (unexcited) state, which is manifested by changes in the dipole moment, polarisability, and geometry of the molecules, by changes in the position of the acid–basic equilibrium, and also by changes in the ionisation potential, electron affinities, etc.[1,4,21,25,33-37].

The free energy ΔG of an electron transfer reaction in the gas phase between donor (D) and acceptor (A) molecules is defined fairly accurately by the relation

$$\Delta G = I_D - E_A, \qquad (1)$$

where I_D is the ionisation potential of the donor and E_A the electron affinity of the acceptor.

On photoexcitation, the ionisation potential I_D diminishes by the excitation energy of the donor $E(^{1,3}D^*)$†, while the electron affinity E_A increases by the excitation energy of the acceptor $E(^{1,3}A^*)$.[33] Thus the free energy ΔG of the photochemical electron transfer, for example between $^{1,3}A^*$ and D, namely

$$^{1,3}A^* + D \rightarrow A^{\bar{}} + D^{\ddagger}, \qquad (I)$$

is defined by the relation

$$\Delta G = I_D - [E_A + E(^{1,3}A^*)]. \qquad (2)$$

If the photoreaction takes place between electrically neutral molecules, the electron transfer results in the formation of the radical-ion pair $A^{\bar{}}D^{\ddagger}$ stabilised by the Coulombic interaction:

$$^{1,3}A^* + D \rightarrow A^{\bar{}}D^{\ddagger}. \qquad (II)$$

In this case the free energy change is

$$\Delta G = I_D - [E_A + E(^{1,3}A^*)] - e^2/R, \qquad (3)$$

where e is the electronic charge and R the distance between the centres of the molecules A and D. Electron transfer in reactions (I) and (II) becomes possible when $\Delta G < 0$.

When the energetics of a photoreaction in solution is considered, one must take into account the energy of the transfer of the molecules $^{1,3}A^*(^{1,3}D^*)$ and A(D), the radical-ion pair $A^{\bar{}}D^{\ddagger}$, and the radical-ions $A^{\bar{}}$ and $D^{\ddagger}$ from the gas to the condensed phase. The energy of the transfer (solvation) of ions (radical-ions) from a vacuum into a medium with a dielectric constant ε is given by the following expression according to Born:

$$\Delta G(A^{\bar{}}) + \Delta G(D^{\ddagger}) = -\frac{e^2}{2}\left(\frac{1}{R_{A^{\bar{}}}} + \frac{1}{R_{D^{\ddagger}}}\right)\left(1 - \frac{1}{\varepsilon}\right), \qquad (4)$$

where $R_{A^{\bar{}}}$ and $R_{D^{\ddagger}}$ are the radii of the radical-ions $A^{\bar{}}$ and $D^{\ddagger}$ respectively. Consequently the free energy of the photochemical electron transfer reaction in solution, leading to the formation of solvated radical-ions as the final products [reaction analogous to reaction (I)] is

$$\Delta G = I_D - [E_A + E(^{1,3}A^*)] - \frac{e^2}{2}\left(\frac{1}{R_{A^{\bar{}}}} + \frac{1}{R_{D^{\ddagger}}}\right)\left(1 - \frac{1}{\varepsilon}\right). \qquad (5)$$

†The superscript 1,3 denotes the multiplicity of the state (singlet, triplet).

The energy of the transfer of an ion (radical-ion) pair, having an effective radius r and a dipole moment μ, from a vacuum into a medium with a dielectric constant ε is given by the following expression according to Kirkwood[38]:

$$\Delta G(A^{\bar{}}D^{+}) \simeq -\frac{\mu^2}{r^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right). \qquad (6)$$

If the photochemical electron transfer involves the formation of a solvated radical-ion pair (exciplex) as the final product, then the free energy of the reaction, analogous to reaction (II), is

$$\Delta G = I_D - [E_A + E(^{1,3}A^*)] - \frac{e^2}{R} - \frac{\mu^2}{r^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right). \qquad (7)$$

For the electron transfer reaction in solution, it is convenient to replace the values of I_D and E_A known for the gas phase by the half-wave potentials for the polarographic reduction of the donor $E_{1/2}(D/D^+)$ and the polarographic reduction of the acceptor $E_{1/2}(A^-/A)$:[39-42]

$$I_D = E_{1/2}(D/D^+) - \Delta G(D^+) + \text{const}, \qquad (8)$$

$$E_A = E_{1/2}(A^-/A^+) + \Delta G(A^-) + \text{const}. \qquad (9)$$

The half-wave potentials are known for many aromatic hydrocarbons[43-48], inorganic compounds[49-52], dyes[53,54], and pigments[25]. The free energy of electron transfer in the photochemical reaction analogous to reaction (I), formulated in terms of the $E_{1/2}$ potentials, is

$$\Delta G = E_{1/2}(D/D^+) - [E_{1/2}(A^-/A) + E(^{1,3}A^*)], \qquad (10)$$

and for a photochemical electron transfer reaction analogous to reaction (II) the free energy is

$$\Delta G = E_{1/2}(D/D^+) - [E_{1/2}(A^-/A) + E(^{1,3}A)] + \frac{e^2}{2}\left(1 - \frac{1}{\varepsilon}\right)\left(\frac{1}{R_{D^{\ddagger}}} + \frac{1}{R_{A^{\bar{}}}}\right) - \frac{e^2}{R} - \frac{\mu^2}{r^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right). \qquad (11)$$

The electrochemical potentials of the molecules in the ground, excited singlet, and excited triplet states.

Substance	$E_{1/2}(D/D^+)$, V	$-E_{1/2}(A^-/A)$, V	$^1E^*$, eV	$^3E^*$, eV	$-[E_{1/2}(D/D^+) - E(^1D^*)]$, V	$-[E_{1/2}(D/D^+) - E(^3D)]$, V	$-E_{1/2}(A^-/A) + E(^1A^*)$, V	$E_{1/2}(A^-/A) + E(^3A^*)$, V
Biphenyl	—	2.65 [48]	4.09 [15]	2.82 [15]	—	—	1.44	0.17
Naphthalene	—	2.58 [48]	3.93 [15]	2.62 [15]	—	—	1.35	0.04
Phenanthrene	—	2.51 [48]	3.58 [15]	2.68 [15]	—	—	1.07	0.17
Anthracene	—	1.96 [48]	3.26 [15]	1.85 [15]	—	—	1.30	−0.11
Tetracene	—	1.53 [48]	2.62 [15]	1.27 [15]	—	—	1.09	−0.26
Chlorophyll *a*	0.54 [25]	1.11 [25]	1.85 [25]	1.33 [25]	1.31	0.79	0.74	0.22
Chlorophyll *b*	0.65 [25]	1.05 [25]	1.91 [25]	1.39 [25]	1.26	0.74	0.86	0.34
Phaeophytin *a*	0.92 [25]	0.84 [25]	1.84 [25]	1.33 [25]	0.92	0.41	1.00	0.49
Bacteriochlorophyll	0.40 [25]	1.08 [25]	1.58 [25]	1.00 [25]	1.18	0.60	0.50	−0.08
Porphin	0.93[25]	1.18 [25]	2.02 [25]	1.56 [25]	1.09	0.63	0.84	0.38
Riboflavin	—	0.61 [25]	2.50 [25]	2.02 [25]	—	—	1.89	1.41
Indole	1.26 [25]	—	4.28 [25]	3.09 [25]	3.02	1.83	—	—
Eosin	0.89 [53]	1.09 [53]	2.33 [53]	1.84 [15]	1.44	0.95	1.24	0.75
Acridine Orange	1.04 [53]	1.13 [53]	2.52 [53]	2.07 [15]	1.48	1.03	1.39	0.94
Thionine	1.27[53]	0.43 [53]	2.05 [53]	1.69 [55]	0.78	0.42	1.62	1.26
Phenosafranine	1.32[53]	0.67 [53]	2.34 [53]	1.77 [22]	1.02	0.45	1.67	1.10
$Ru(bipy)_3^{2+}$	1.29 [25]	1.33 [25]	—	2.10 [25]	—	0.81	—	0.77

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

In particular, it follows from Eqn.(10) that the polarographic reduction potential increases (the polarographic oxidation potential decreases) by the electronic excitation energy.

The Table lists the values of $E_{1/2}$ and $E(^{1,3}A^*, ^{1,3}D^*)$ for a series of compounds. Thus the condition for reaction (I) in solution is the inequality

$$E_{1/2}(D/D^+) - E_{1/2}(A^-/A) - E(^{1,3}A^*) < 0. \quad (12)$$

The above relation is convenient for assessing the possibility of the electron transfer reaction in a specific system $^{1,3}A^*$–D.

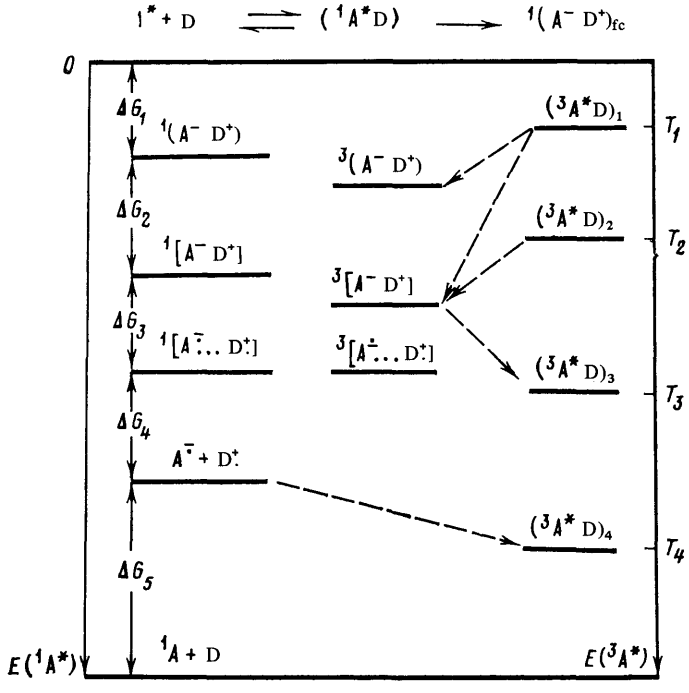


Figure 1. The energy scheme for electron transfer in a photochemical reaction between an acceptor A* and a donor D (for explanation, see text).

The efficiency of the formation of the final products of the electron transfer reaction is determined mainly by the energetics of the intermediate stages. Fig.1 presents a generalised energy scheme for electron transfer between the molecules of the acceptor $^{1,3}A^*$ and the donor D#. The electron transfer process involving the formation of solvated radical-ions includes the following sequence of stages.

1. The formation of a collision complex $^1A^*D$ between the excited singlet molecule $^1A^*$ and the molecule D in the ground state as a result of diffusional collisions between $^1A^*$ and D:

$$^1A^* + D \rightleftharpoons (^1A^*D). \quad (III)$$

Reaction (III) competes with the intersystem crossing into the triplet state $^3A^*$ and also with fluorescence and internal conversion processes. The free energy of reaction (III) is

$$\Delta G = -RT \ln \Delta V, \quad (13)$$

where ΔV is the relative change in the volume on formation of the complex[48].

#The reasoning remains the same when one considers the electron transfer reaction between $^{1,3}D^*$ and A.

2. Adiabatic electron transfer in the complex ($^1A^*D$) with formation of a vibrationally excited charge transfer state $^1(A^-D^+)_{fc}$ (the Franck–Condon state).

3. Vibrational relaxation from $^1(A^-D^+)_{fc}$ to the thermalised state $^1(A^-D^+)$ which takes place over a period of 10^{-12} s with retention of the initial orientation of the solvent molecules. The thermalised radical-ion pair in the triplet state $^3(A^-D^+)$ can be formed under the following conditions: (1) the transition to the triplet state T_1 competes effectively with the quenching of the fluorescence of $^1A^*$ by the donor molecules D; (2) the triplet level T_1 lies above the level corresponding to the charge transfer state $^3(A^-D^+)$. The free energy change ΔG_1 (Fig.1) is

$$\Delta G_1 = E_{1/2}(D/D^+) - [E_{1/2}(A^-/A) + E(^1A^*)] + \frac{e^2}{2}\left(\frac{1}{R_{D^+}} + \frac{1}{R_{A^-}}\right)\left(1 - \frac{1}{\varepsilon}\right) - \frac{e^2}{R} - \frac{\mu^2}{r^3}\left(\frac{n^2-1}{2n^2+1}\right), \quad (14)$$

where n is the refractive index of the medium. Thus a necessary condition for the quenching of the fluorescence (or the triplet state) of the acceptor by the electron donor is $\Delta G_1 < 0$.

4. The reorientation of the solvent molecules around the radical-ion pair $^1(A^-D^+)$ over a period 10^{-11}–10^{-10} s with formation of a radical-ion pair $^1[A^-D^+]$ (exciplex) stabilised by solvent molecules. The radical-ion pair $^3[A^-D^+]$ can be formed via the triplet state, pathways involving both $(^3A^*D)_1$ and $(^3A^*D)_2$ being energetically feasible under these conditions. However, electron transfer via the T_2 state is less probable, because it requires a definite orientation of the solvent molecules around the radical-ion pair $^3[A^-D^+]$. The solvation process can lead to the formation of solvate-separated radical-ion pairs $^1[A^-...D^+]$ and $^3[A^-...D^+]$ stabilised by the Coulombic interaction arising between the radical-ions A and D. The free energy changes ΔG_2 and ΔG_3 are

$$\Delta G_2 = -\frac{\mu^2}{r^3}\left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right), \quad (15)$$

$$\Delta G_3 = -\frac{e^2}{2}\left(\frac{1}{R_{D^+}} + \frac{1}{R_{A^-}}\right)\left(1 - \frac{1}{\varepsilon}\right) - \frac{e^2}{\varepsilon a} + \frac{e^2}{R} + \frac{\mu^2}{r^3}\left(\frac{\varepsilon-1}{2\varepsilon+1}\right), \quad (16)$$

where a is the distance between A^- and D^+ in the solvate-separated radical-ion pair.

5. In polar media the solvate-separated radical-ion pair dissociates into solvated radical-ions and the free energy of the reaction is

$$\Delta G_4 = e^2/\varepsilon a. \quad (17)$$

6. The formation of radical-ion pairs in the triplet state $^3[A^-D^+]$ and $^3[A^-...D^+]$ from the triplet state T_3 is energetically unlikely and requires an activation energy.

7. The recombination of radical-ions can lead to the population of the triplet level T_4 subject to the condition that

$$E_{1/2}(D/D^+) - E_{1/2}(A^-/A) > T_4. \quad (18)$$

The above relations (14)–(18) make it possible to find the free energies of the corresponding processes and hence to reach a conclusion about their feasibility.

III. THE QUENCHING OF THE EXCITED STATE AS A RESULT OF ELECTRON TRANSFER

The electron transfer in photochemical reactions between molecules, for example, those of the acceptor ($^{1,3}A^*$) and donor (D), can occur both as a result of diffusional collisions between $^{1,3}A^*$ and D and within the excited

complex formed beforehand by non-excited molecules A and D. The mechanism of the electron transfer reactions occurring as a result of the diffusional collisions between $^{1,3}A^*$ and D is considered below, it being assumed that a complex between A and D is not formed.

The electron transfer in a photochemical reaction between organic compounds can proceed both via excited singlet and the triplet state of the partners. The interaction between $^{1,3}A^*$ and D inevitably leads to the appearance of an additional pathway to the degradation of the excitation energy of the molecule $^{1,3}A^*$ and electron transfer results in a decrease of the lifetime of the excited molecules in the presence of a quenching additive. For the reaction between excited singlet acceptor molecules $^1A^*$ and non-excited donor molecules D,

$$^1A^* + D \xrightarrow{k_q^S} A^- + D^+, \qquad (IV)$$

the decrease of the lifetime of the molecules $^1A^*$ in the presence of D obeys the Stern–Volmer equation

$$\tau_S^0/\tau_S = 1 + k_q^S \tau_S^0 [D], \qquad (19)$$

where τ_S^0 and τ_S are the lifetimes of the excited singlet molecules $^1A^*$ in the absence and presence of the donor molecules respectively. For the reaction between triplet acceptor molecules $^3A^*$ and non-excited donor molecules D,

$$^3A^* + D \xrightarrow{k_q^T} A^- + D^+, \qquad (V)$$

the decrease of the lifetime of the triplet acceptor molecules in the presence of the quenching additive D is described by an equation analogous to Eqn.(19), k_q^S and k_q^T being the quenching rate constants for the corresponding states.

Thus the experimental observation of a linear relation between the relative decrease of the lifetime of excited molecules and the concentration of the quenching additive indicates directly the feasibility of the electron transfer. However one should note that not every quenching process of the excited states $^{1,3}A^*$ under the influence of the additive D, described quantitatively by Eqn.(19), is due to the electron transfer reaction (IV) or (V). A relation of the Stern–Volmer type holds also for many other processes, for example, for the triplet–triplet energy transfer between the acceptor and donor and the transfer of a hydrogen atom between $^{1,3}A^*$ and D. The electron transfer reaction is characterised, firstly, by the formation of an exciplex (in media of low polarity), secondly, by the formation of solvated radical-ions (in polar media), and, thirdly, by the existence of a correlation between the efficiency of the quenching of the excited state and the electron-donating (electron-accepting) properties of the quenching agent.

A definite relation can be established between the quenching rate constants $k_q^S(k_q^T)$ and the electron-donating properties of the quenching agent. In polar media the electron transfer in the collision complex between the excited acceptor molecule and the molecule of the donor quenching agent leads to the formation of a solvate-separated radical-ion pair and is described by the following scheme[56]:

Scheme 1

$$\begin{array}{ccccc} ^{1,3}A^* + D & \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} & (^{1,3}A^*D) & \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} & ^{1,3}[A^- \ldots D^+], \\ {\scriptstyle 1/\tau_{S,T}^0}\downarrow & & & & \downarrow{\scriptstyle k_{30}} \end{array}$$

where k_{12}, k_{21}, k_{23}, k_{32}, and k_{30} are the rate constants for the corresponding processes. It follows from Scheme 1 that

$$k_q^S \ (\text{or} \ k_q^T) = \frac{k_{12}}{1 + (1 + k_{32}/k_{30})\, k_{21}/k_{23}}. \qquad (20)$$

Eqn.(20) can be formulated in the following way:

$$k_q^S, k_q^T = k_{12}/\left[1 + \frac{k_{12}}{K_p k_{30}}\left(e^{\Delta G_{23}^{\ddagger}/RT} + e^{\Delta G_{23}/RT}\right)\right], \qquad (21)$$

where $\Delta G_{23}^{\ddagger}$ is the free energy of activation, ΔG_{23} the free energy of electron transfer in the collision complex, and $K_p = k_{12}/k_{21}$ the equilibrium constant.

$\Delta G_{23}^{\ddagger}$ and ΔG_{23} are related:

$$\Delta G_{23}^{\ddagger} = \Delta G_{23}/2 + [(\Delta G_{23}/2)^2 + (\Delta G_{23}^{\ddagger}(0))^2]^{1/2}, \qquad (22)$$

where $\Delta G_{23}^{\ddagger}(0)$ is the free energy of activation for $\Delta G_{23} = 0$.

Eqn.(21) can be simplified in the following two cases.

1. $\Delta G_{23} \ll 0$ and $\Delta G_{23}^{\ddagger} \cong 0$, whereupon

$$k_q^S \ (\text{or} \ k_q^T) = k_{12}/(1 + k_{21}/k_{30}). \qquad (23)$$

In this case the quenching rate constants k_q^S and k_q^T are invariant and independent of the nature of the donor quenching agent. It has been shown[56] that the ratio $k_{21}/k_{30} < 1$ for the electron transfer reaction between excited singlet molecules of a number of aromatic hydrocarbons (anthracene, 3,4-benzacridine, etc.) and electron donor molecules (tetramethyl-*p*-phenylenediamine, diethylaniline, methyldiphenylamine, etc.) and, in conformity with Eqn.(23), the rate constant for the quenching of the fluorescence is virtually identical with the constant k_{12} determined by the diffusion of the reacting molecules.

2. $\Delta G_{23} \gg 0$ and $\Delta G_{23}^{\ddagger} \cong \Delta G_{23}$, whereupon

$$k_q^S (\text{or} \ k_q^T) = \frac{K_p k_{30}}{2} e^{-\Delta G_{23}/RT}; \qquad (24)$$

according to Eqn.(24), there should be a linear relation between $\ln k_q^S$, $\ln k_q^T$, and ΔG_{23}. Figs.2*a* and 2*b* present the relations between k_q^S and ΔG_{23} for the reaction between aromatic hydrocarbons and electron donors[56] and between k_q^T/k_{12} and ΔG_{23} for the reaction between thionine and electron donors[57]. Fig.2 shows, firstly, that the values of k_q^S and k_q^T are constant over a wide range of values of ΔG_{23}, starting from $\Delta G_{23} < 10$ kcal mol^{-1} and, secondly, that the values of $\ln k_q^S$ and $\ln k_q^T$ are directly proportional to ΔG_{23}, starting from $\Delta G_{23} > 3$ kcal mol^{-1}. Thus Fig.2 illustrates a satisfactory agreement between the experimental data and the results of the theoretical study of Eqns.(21) to (24).

Relations similar to those presented in Fig.2 have also been obtained for the quenching of the fluorescence of pyrene and anthracene by a number of electron acceptors[58], of rubicene and acridine by certain amines[59,60], of substituted naphthalenes by dienes[61], of aromatic hydrocarbons and azastilbenes by inorganic anions[49,52,62], of bipyridyl complexes of ruthenium by nitro-compounds[63] and organic electron donors[64], of uranyl ions by metal cations[65], etc. The quenching of triplet states via the electron transfer mechanism [in conformity with Eqns.(23) and (24)] has been demonstrated for 2-naphthol[66], benzophenone[67], duroquinone[68], Methylene Blue[69,70], a number of aromatic hydrocarbons and carbonyl compounds[71], and also chlorophyll[72,73].

In non-polar media electron transfer also takes place in the collision complex between an excited molecule, for example, an acceptor molecule, and a non-excited donor molecule and

leads to the formation of a solvated radical-ion pair (exciplex). In this case the electron transfer is analogous to Scheme 1 (the difference consists in the replacement of the solvate-separated radical-ion pair by the exciplex) and the expressions for the rate constants for the quenching of the excited singlet and triplet states are analogous to Eqns.(20), (21), (23), and (24). The relations between $\ln k_q^S$ and $\ln k_q^T$, on the one hand, and ΔG_{23}, on the other ($\Delta G'_{23}$ is the free energy of the electron transfer reaction in the collision complex with formation of an exciplex), are similar to those presented in Fig.2.[73-75]

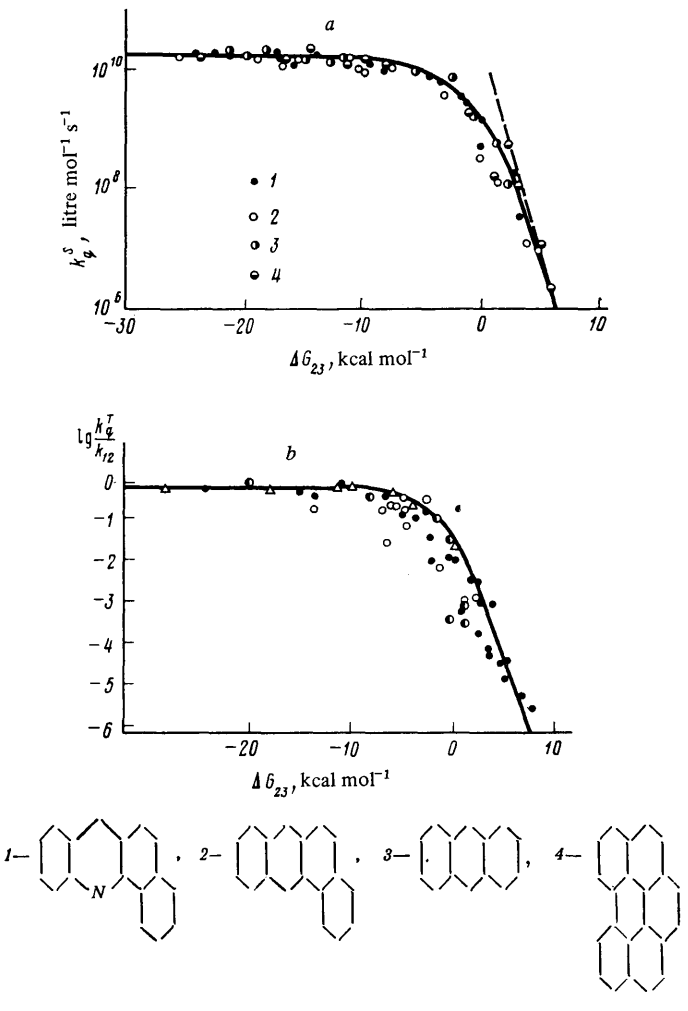


Figure 2. Dependence of the rate constants for (*a*) the quenching of the fluorescence of aromatic hydrocarbons[56] and (*b*) the quenching of the triplet state of Thionine[57] on the change in the free energy ΔG_{23}.

ΔG_{23} can be expressed in terms of the polarographic oxidation potential of the donor and the polarographic reduction potential of the acceptor:

$$\Delta G_{23} = E_{1/2}(D/D^+) - E_{1/2}(A^-/A) - E(^{1,3}A^*) - e^2/\varepsilon a. \quad (25)$$

The variation of the quenching rate constant with the donor oxidation potential (or the acceptor reduction potential for the photochemical oxidation of the donor) is analogous to that shown in Fig.2.

Two consequences which follow from an examination of Eqn.(23) and (24) must be mentioned. Firstly, according to Eqn.(23), the constants k_q^S and k_q^T can differ as a consequence of the difference between the rate constants for the destruction of the singlet and triplet radical-ion pairs (k_{30}). For the triplet pair, k_{30} should be appreciably smaller than for the singlet pair because the transition from the triplet pair to the ground state of the initial reaction products is forbidden[76-78]. Secondly, it follows from Eqn.(24) that the constants k_q^S and k_q^T must differ because of the difference between the values of ΔG_{23} for the reaction proceeding via the excited singlet and triplet states respectively:

$$\ln(k_q^S/k_q^T) = \ln(k_{30}^S/k_{30}^T) + \frac{1}{RT}[E(^1A^*) - E(^3A^*)]. \quad (26)$$

Thus the study of the kinetics and thermodynamics of the electron transfer process in photochemical reactions makes it possible to account for the quenching of the excited state by electron donors and acceptors as a consequence of electron transfer and to find the oxidation (reduction) potentials of the quenching agent molecules from the rate constant for the quenching of the excited state.

IV. THE NATURE OF THE EXCITED STATE OF THE MOLECULES INVOLVED IN THE ELECTRON TRANSFER REACTION

Electron transfer with participation of both excited singlet and triplet molecular states is energetically feasible.

1. Electron Transfer with Participation of the Triplet State

In liquid solutions electron transfer takes place as a result of diffusional collisions between the excited molecule and the other molecule involved in the reaction. The number of "acceptor" collisions is determined by the number of collisions between the reacting species during the lifetime of the excited states. The relation between the relative yield of the electron transfer reaction product, the lifetime of the excited state, and the concentration of the reactant D can be established for the reactions

$$^{1,3}A^* + D \xrightarrow{k_r} A^- + D^+, \quad (VI)$$

$$^{1,3}A^* \xrightarrow{k_0} A, \quad (VII)$$

where k_r is the effective rate constant for the electron transfer and k_0 the rate constant for the deactivation of the excited state $^{1,3}A^*$.

If the lifetime of the product exceeds significantly the duration of the electron transfer reaction, then the following relation exists between the initial concentration of the excited molecules $[^{1,3}A^*]_0$ and the maximum concentration $[A^-]_{max}$:

$$[A^-]_{max} = [^{1,3}A^*]_0(1 + k_0/k_r[D])^{-1}, \quad (27)$$

from which it follows that the maximum concentration of A^- is greatest for the condition $k_0 \ll k_r[D]$ and smallest for $k_0 \gg k_r[D]$. Typical rate constants for the excited singlet states of the molecules of many organic substances are $k_r \cong 10^9$ litre mol^{-1} s^{-1} and $k_0 \cong 2 \times 10^8$ s^{-1}. In this case the maximum yield of the electron transfer reaction products is

attained at concentrations of the quenching agent [D] > 1 M. Typical rate constants for the triplet states of molecules are $k_\gamma \cong 10^8$ litre mol^{-1} s^{-1} and $k_0 \cong 10^3$ s^{-1}; for these values, the maximum yield of $A^{\overline{\cdot}}$ (or $D^{\overset{+}{\cdot}}$) is attained at donor concentrations [D] > 10^{-4} M.[15,21]

Thus it follows from the results presented that, as a consequence of the significant difference between the lifetimes of the excited singlet and triplet molecules, the electron transfer at low concentrations of the quenching agent can proceed only via the triplet state. The proof of the involvement of the triplet state in the electron transfer reaction is based on a series of experimental data.

1. The quenching of the T state by electron acceptors (donors). To some extent, the quenching rate constant reflects the reactivity of the triplet states. The constant is found from data for the quenching of the triplet–triplet absorption.

2. Comparison of the emission times of a pulsed photoexcitation source and the time required for the accumulation of the electron transfer products. If the reaction proceeds via the triplet state and, according to the experimental conditions, the pulsed photoexcitation time τ_{pep} is significantly shorter than the lifetime of the triplet state τ_T, then the time of the attainment of the maximum concentration τ_{max} of the radical-ions at low concentrations of the quenching agent (electron acceptor or donor) must satisfy the condition

$$\tau_{pep} < \tau_{max} \leqslant \tau_T. \qquad (28)$$

If the radical-ions are formed with participation of the excited singlet state, then the maximum concentration of the radical-ions is attained during the photopulse ($\tau_{max} \cong \tau_{pep}$).

3. The competitive quenching of the triplet state. It follows from Eqns.(VI) and (VII) that, in the presence of a competitive quenching agent for the T state, the quantum yield of the radical-ions $\phi_{A^{\overline{\cdot}},D^{\overset{+}{\cdot}}}$ decreases in accordance with the equation

$$\varphi_{A^{\overline{\cdot}},D^{\overset{+}{\cdot}}} = \varphi^0_{A^{\overline{\cdot}},D^{\overset{+}{\cdot}}} (1 + k_Q \tau^0_T [Q])^{-1}, \qquad (29)$$

where $\phi^0_{A^{\overline{\cdot}},D^{\overset{+}{\cdot}}}$ and τ^0_T are quantities determined in the absence of the competitive quenching agent Q. The competitive quenching agents can be compounds with heavy atoms as well as compounds which function as acceptors of the triplet excitation energy, for example, oxygen, etc.[79].

Extensive factual data, demonstrating convincingly that the electron transfer takes place via the triplet states of the molecules of many organic compounds, have now accumulated. The involvement of triplet states has been demonstrated in the reduction of pyrene by radical-anions ($CO_2^{\overline{\cdot}}$, $CH_2O^{\overline{\cdot}}$, $CH_3CHO^{\overline{\cdot}}$),[80] of 2-naphthol and 1-anthrol by quinoline and 4-methylpyridine,[81] of 4-nitropyridine by isopropyl alcohol[82], of benzophenone and 2-naphthaldehyde by amines[83–86], and of quinones by amines and Fe^{2+},[87,88] and in the photochemical oxidation of phenothiazine by nitrobenzene[89] and Eu^{3+}.[90] The important role of the triplet state has also been demonstrated in one-electron reduction and oxidation reactions of dyes and photosynthetic pigments: Thionine[91–95], Methylene Blue[60,69,96–104], fluorescein[105–108], eosin[109–111], erythrosin[21], safranine T,[112] phenosafranine[113], oxonin[114], Acridine Orange[115], rhodamine 6G,[116–118], polymethine dyes[119,120], chlorophyll[22,121–130], phaeophytin[131], Mg-phthalocyanine[132], porphyrins[133], etc.

The above examples illustrate the electron transfer reaction occurring as a result of diffusional collisions between a triplet donor (acceptor) molecule and a non-excited molecule of the other reactant (exogenic electron acceptor or donor respectively). At the same time electron transfer can proceed with participation of molecular triplet states also in the absence of extraneous electron donor or acceptor molecules. In this case the other reactant may be a molecule in the triplet state (triplet–triplet interaction) or in a non-excited state (concentration-dependent quenching):

$$^3A^* + {}^3A^* \rightarrow A^{\overline{\cdot}} + A^{\overset{+}{\cdot}}, \qquad (VIII)$$

$$^3A^* + {}^1A \rightarrow A^{\overline{\cdot}} + A^{\overset{+}{\cdot}}. \qquad (IX)$$

Measurements of the rate of accumulation of radical-ions formed via reactions (VIII) and (IX) have shown that the rate constants for the accumulation of $A^{\overline{\cdot}}$ are always smaller than the rate constants for the quenching of the triplet state as a result of the triplet–triplet interaction and the concentration-dependent quenching[19,21,111]. Consequently the electron transfer reactions (VIII) and (IX) are accompanied by processes involving the "physical" deactivation of the triplet states:

$$^3A^* + {}^3A^* \rightarrow {}^1A^* + {}^1A, \qquad (X)$$

$$^3A^* + {}^1A \rightarrow {}^1A + {}^1A. \qquad (XI)$$

The feasibility of electron transfer via reactions (VIII) and (IX) can be assessed with the aid of the relations

$$E_{1/2}(A/A^+) - E_{1/2}(\overline{A}/A) - 2E(^3A^*) < 0, \qquad (30)$$

$$E_{1/2}(A/A^+) - E_{1/2}(A^-/A) - E(^3A^*) < 0. \qquad (31)$$

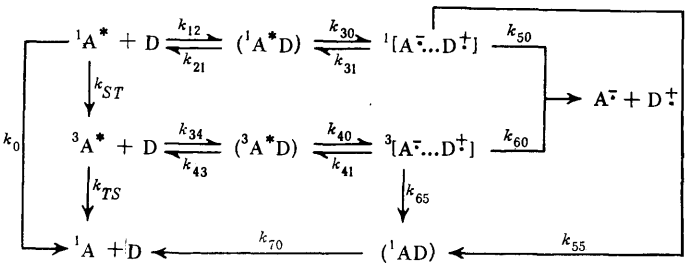
For example, the polarographic oxidation and reduction potentials are respectively +0.76 and −0.99 V for chlorophyll *a* in the $^3E^* = 1.33$ eV triplet state (see Table). Thus, in conformity with Eqns.(30) and (31), the electron transfer can occur only when two triplet chlorophyll *a* molecules interact. The detection of the pigment radical-ions has been confirmed by[134] measurements of the transient conductivity arising on pulsed photoexcitation of chlorophyll solutions. The occurrence of electron transfer via reactions (VIII) and (IX) has been established for fluorescein[105], eosin[135], rhodamine 6G,[116,118] and thiazine[97,111] and polymethine dyes[120,136].

2. Kinetic Analysis of the Electron Transfer Reaction Mechanism

With increase in the concentration of the quenching additive, the number of "successful" collisions not only between triplet and quenching agent molecules but also between excited singlet and quenching agent molecules also increase. Consequently at certain concentrations of the quenching agent there is a possibility of electron transfer involving the excited singlet states of the molecules and leading to the formation of radical-ions. The formation of radical-ions as a result of electron transfer between the excited molecule of, for example, the acceptor and the non-excited molecule of the donor occurs only in polar media. The dependence of the quantum yield in the formation of radical-ions on the concentration of the quenching agent in the electron transfer reaction, proceeding through excited

singlet and triplet states of the acceptor in conformity with Scheme 2, is analysed below:

Scheme 2



It is suggested that a complex is not formed between the acceptor and donor molecules; k_0 and k_{ST} are the rate constants for the fluorescence (including internal conversion) and the intercombination conversion to the triplet state respectively and k_{TS} is the rate constant for the intercombination degradation.

For a reaction proceeding similarly via the excited singlet state, there is a linear relation between the reciprocal of the quantum yield in the formation of solvated radical-ions ($A^{\bar{\cdot}}$ or $D^{+\cdot}$) and the reciprocal of the donor concentration:

$$\frac{1}{\varphi^{S}_{A^{\bar{\cdot}},D^{+}}} = 1 + \frac{k_{55}}{k_{50}} + \left(1 + \frac{k_{55}}{k_{50}}\right)\frac{1}{k_q^S \tau_S^0 [D]}, \qquad (32)$$

where

$$k_q^S = k_{12}/\left[1 + \frac{k_{21}}{k_{30}}\left(1 + \frac{k_{31}}{k_{50} + k_{55}}\right)\right], \qquad (33)$$

$$\tau_S^0 = (k_0 + k_{ST})^{-1}. \qquad (34)$$

For a reaction proceeding solely via the triplet state (when the excited singlet state is quenched), the dependence of the quantum yield in the formation of solvated radical-ions ($A^{\bar{\cdot}}$ or $D^{+\cdot}$) on 1/[D] passes through a minimum in conformity with the relation

$$1/\varphi^{(T)}_{A^{\bar{\cdot}},D^{+}} = \left(\frac{1 + k_{65}/k_{60}}{\varphi_T}\right)\left(1 + \frac{k_q^S \tau_S^0}{k_q^T \tau_T^0} + k_q^S \tau_S^0 [D] + \frac{1}{k_q^T \tau_T^0 [D]}\right). \qquad (35)$$

where

$$k_q^T = k_{34}/\left[1 + \frac{k_{43}}{k_{40}}\left(1 + \frac{k_{41}}{k_{60} + k_{65}}\right)\right], \qquad (36)$$

$$k_q^S = k_{12}/\left[1 + \frac{k_{21}}{k_{30}}\left(1 + \frac{k_{31}}{k_{55}}\right)\right], \qquad (37)$$

$$\varphi_T = \frac{k_{ST}}{k_0 + k_{ST}}, \qquad (38)$$

$$\tau_T^0 = k_{TS}^{-1}. \qquad (39)$$

Relations (32) and (35) have been obtained for the electron transfer reaction between an excited acceptor molecule and a non-excited donor molecule. Exactly the same expressions for the reciprocals of the quantum yield in the formation of the radical-ions can be obtained for the electron transfer reaction between an excited donor molecule and a non-excited acceptor molecule. Fig.3 illustrates the the relations between $1/\phi^{(S,T)}_{A^{\bar{\cdot}},D^{+\cdot}}$ and 1/[D] expected according to Eqns.(32) and (35) and corresponding to the values $\phi_T \cong 0.5$, $k_q^S \cong 10^{10}$ litre mol^{-1} s^{-1}, $k_q^T \cong 10^9$ litre mol^{-1} s^{-1} (it is suggested that $\Delta G_{30,40} \ll 0$), $\tau_S^0 \cong 10^{-9}$ s, $\tau_T^0 \cong 10^{-4}$ s, $k_{65}/k_{60} \cong 1$, and $k_{55}/k_{50} \cong 10-10^2$ typical for dyes and pigments. Fig.3 also presents experimental data obtained for the photochemical oxidation of chlorophyll *a* by nitrobenzene. Comparison of the experimental relation with relations (32) and (35) shows that radical-ions are formed solely via the triplet state.

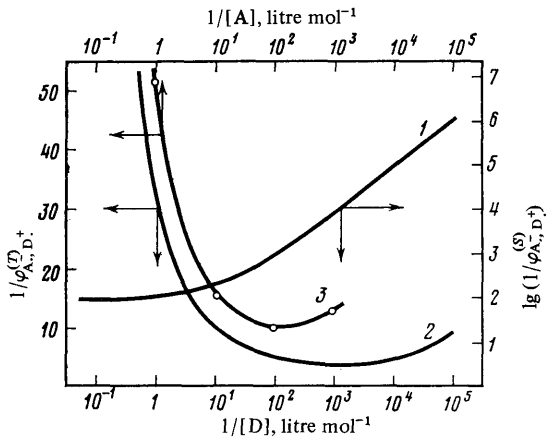
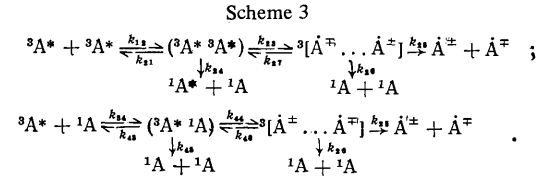


Figure 3. Dependence of the reciprocal of the quantum yield for the formation of radical-ions on the reciprocal of the concentration of the excited state quenching agent: *1*) and *2*) according to Eqns.(32) and (35); *3*) experimental data for the photochemical oxidation of chlorophyll with nitrobenzene[128].

Thus the conclusion that the triplet state plays an important role in the formation of electron transfer products is based on the kinetic analysis of the reaction mechanism postulating the quenching of both the excited singlet and triplet states. This conclusion has been confirmed in direct experiments on the electron transfer between an excited bacteriophaeophytin molecule and *p*-benzoquinone by the method of picosecond spectrophotometry[137].

As stated above, electron transfer can occur as a result of the interaction of both two triplet molecules with one another and of a triplet molecule with a non-excited molecule. The electron transfer reactions and the competing processes are presented in Scheme 3 below:

Scheme 3



Measurements of the rate constants for the quenching of the triplet state as a result of the triplet–triplet interaction [$k_q^{(T-T)}$] and the concentration-dependent quenching [$k_q^{(T-S)}$] have shown that $k_q^{(T-T)}$ exceeds $k_q^{(T-S)}$: in terms of order of magnitude, $k_q^{(T-T)} \cong 10^9$ litre

mol^{-1} s^{-1} and $k_q^{(T-S)} \cong 10^7-10^8$ litre mol^{-1} s^{-1}.[19,21,111,118,120] The difference between $k_q^{(T-T)}$ and $k_q^{(T-S)}$ can be explained in terms of Scheme 3, from which it follows that

$$k_q^{T-T} \simeq k_{12}/(1+k_{21}/k_{23}) + k_{12}/2(1+k_{23}/k_{21}). \quad (40)$$

Eqn.(40) has been obtained on the assumption that $k_{27} < (k_{25}+k_{26})$, since $\Delta G_{23} < -20$ kcal mol^{-1} [in conformity with tabulated data and Eqn.(30)] and $k_{24} < k_{23}$, k_{21}. It also follows from Scheme 3 that

$$k_q^{(T-S)} \simeq \frac{k_{34}}{2k_{43}/k_{44}} + \frac{k_{34}}{k_{43}/k_{45}}. \quad (41)$$

Eqn.(41) has been obtained on the assumption that $k_{46} \cong k_{25}+k_{26}$ [$\Delta G_{44} > 2-5$ kcal mol^{-1} in conformity with the tabulated data and Eqn.(31)], and $k_{43} > k_{45}$, k_{44}. Since $k_{12}=k_{34}$ and $k_{21}=k_{43}$, the differences between $k_q^{(T-T)}$ and $k_q^{(T-S)}$ are due to the fact that $k_{44} < k_{23}$. Measurements of the rate constants for electron transfer as a result of the triplet–triplet interaction [$k_r^{(T-T)}$] and the concentration-dependent quenching [$k_r^{(T-S)}$] have shown that $k_r^{(T-T)}$ exceeds $k_r^{(T-S)}$.[21,118,120] The explanation of this finding follows from an examination of Scheme 3.

When account is taken of the above assumptions, Scheme 3 leads to

$$k_r^{(T-T)} = \frac{k_{12}}{(1+k_{21}/k_{23})(1+k_{26}/k_{25})}, \quad (42)$$

$$k_r^{(T-S)} = \frac{k_{34}}{2(k_{43}/k_{44})(1+k_{26}/k_{25})}. \quad (43)$$

Thus the efficiency of electron transfer via the triplet–triplet interaction and concentration-dependent quenching mechanisms is determined by processes occurring in the radical-ion pairs.

Radical-ion pairs are formed in the electron transfer reaction (Scheme 2) exclusively via the triplet state. The explanation of the important role of the triplet state consists in the different rates of the recombination processes occurring in the singlet and triplet radical-ion pairs respectively. According to Scheme 2, electron transfer takes place in the collision complexes formed by the donor molecule with an excited singlet or triplet acceptor molecule. This leads to the formation of radical-pairs in the singlet and triplet states respectively. The probability of the dissociation of the radical-ion pairs into solvated radical-ions is determined by the ratios $k_{50}/(k_{31}+k_{50}+k_{55})$ (for the pair in the singlet state) and $k_{60}/(k_{41}+k_{60}+k_{65})$ (for the pair in the triplet state). For exothermic electron transfer reactions ($\Delta G < -10$ kcal mol^{-1}), the constants k_{31} and k_{41} make a small contribution to the overall rate constant for the destruction of radical-ion pairs and in addition it is evident that $k_{50} \cong k_{69}$.

Thus the ratio of the probabilities of the dissociation of the singlet and triplet radical-ion pairs into radical-ions is $(k_{60}+k_{65})/(k_{50}+k_{55})$. As a consequence of the prohibition of transitions between states of different multiplicity, it is to be expected that $k_{55} \gg k_{65}$ and in addition that $k_{50} < k_{55}$, since the dissociation of the ion pair into radical-ions involves the overcoming of Coulombic interaction forces. Consequently the recombination process, taking place effectively in the singlet pair, significantly suppresses the dissociation of the singlet pair, in contrast to the pair in the triplet state. Thus, according to Gouterman and Holten[77], radical-ions are formed in the photochemical oxidation of bacteriophaeophytin by *p*-benzoquinone exclusively via the triplet state, which has been confirmed in the study of the rate constants for the processes: $k_{55} \cong 10^{12}$, $k_{50} \cong k_{60} \cong 4 \times 10^9$, and $k_{65} \ll 4 \times 10^9$ s^{-1}.

V. THE REACTIVITY OF THE EXCITED STATE IN THE ELECTRON TRANSFER REACTION

The formation of radical-ions in the photochemical electron transfer reaction is a multistage process. The electron transfer takes place in the collision complex formed by excited molecules and a non-excited molecule of the other reactant and leads to the formation of a radical-ion pair. The rate constant k_{23} in Scheme 1 can serve as a measure of the reactivity of the excited state in the electron transfer reaction.

The reactivities of the excited singlet and triplet states are compared below. According to Scheme 2, the electron transfer rate constants can be expressed in the form

$$k_{30} \propto \exp\left(-\Delta G_{30}^{\neq}/RT\right), \quad (44)$$

$$k_{40} \propto \exp\left(-\Delta G_{40}^{\neq}/RT\right), \quad (45)$$

where $G_{30,40}^{\neq}$ is the free energy of activation for electron transfer via the excited singlet and triplet states respectively.

It follows from Eqns.(44) and (45) that the expression

$$\ln(k_{30}/k_{40}) = (\Delta G_{40} - \Delta G_{30})/RT, \quad (46)$$

is valid for endothermic reactions ($\Delta G_{30,40} \gg 0$) when account is taken of Eqn.(22), whereupon $\Delta G_{30,40}^{\neq} \cong \Delta G_{30,40}$. Since

$$(\Delta G_{40} - \Delta G_{30}) = E(^1A^*) - E(^3A^*) \equiv \Delta E, \quad (47)$$

we have

$$\ln(k_{30}/k_{40}) = \Delta E/RT. \quad (48)$$

Thus the greater energy of the excited singlet state of the molecule compared with that of the triplet state is responsible for the greater reactivity of the excited singlet molecules. For an exothermic reaction, where $\Delta G_{30,40} \ll 0$ and $\Delta G_{30,40}^{\neq} \cong 0$, the difference between k_{30} and k_{40} is significantly reduced.

1. Protonation of the Excited State and Comparative Reactivity

Electron transfer can proceed with participation of both protonated (for example, $^{1,3}A^*H^+$) and deprotonated ($^{1,3}A^*$) molecules. The rate constant for the quenching of the excited state is related to the free energy of reaction; consequently there is a relation between the free energy of the electron transfer reaction and the protolytic equilibrium constant for molecules in the excited state. The electron transfer reactions involving deprotonated and protonated excited molecules are presented in Scheme 4:

Scheme 4

$$\begin{array}{ccc} {}^{1,3}A^*H^+ + D & \rightarrow & AH + D^+ \\ \downarrow\uparrow H^+ & & \downarrow\uparrow H^+ \\ {}^{1,3}A^* + D & \rightarrow & A^- + D^+ \end{array}$$

The expressions for the free energy of the electron transfer reaction are

$$\Delta G_b = E_{1/2}(D/D^+) - [E_{1/2}(A^-/A) + E(^{1,3}A^*)], \quad (49)$$

$$\Delta G_a = E_{1/2}(D/D^+) - [E_{1/2}(AH/AH^+) + E(^{1,3}A^*H^+)]; \quad (50)$$

where subscripts a and b denote the protonated and deprotonated states of the acceptor molecules respectively. It follows from Eqns.(49) and (50) that

$$\Delta\Delta G = (\Delta G_b - \Delta G_a) = [E_{1/2}(\mathrm{AH/AH^+}) - E_{1/2}(\mathrm{A^-/A})] + [E(^{1,3}\mathrm{A^*\,H^+}) - E(^{1,3}\mathrm{A^*})]. \quad (51)$$

Scheme 5 below (the Forster cycle)

Scheme 5

$$\begin{array}{ccc} {}^{1,3}\mathrm{A^*} + \mathrm{H^+} & \overset{pK^*}{\rightleftharpoons} & {}^{1,3}\mathrm{A^*\,H^+} \\ \uparrow h\nu_1 & & \uparrow h\nu_2 \\ \mathrm{A} + \mathrm{H^+} & \overset{pK}{\rightleftharpoons} & \mathrm{AH^+} \end{array}$$

leads to the relation

$$E(^{1,3}\mathrm{A^*\,H^+}) - E(^{1,3}\mathrm{A^*}) = 2.3RT(pK - pK^*), \quad (52)$$

where pK and pK^* refer to the acid–base equilibria involving the non-excited and excited (singlet and triplet) molecules (according to Scheme 5)[15]. Scheme 6

Scheme 6

$$\begin{array}{ccc} \mathrm{A^-} + \mathrm{H^+} & \overset{pK_R}{\rightleftharpoons} & \mathrm{\dot{A}H} \\ \uparrow e & & \uparrow e \\ \mathrm{A} + \mathrm{H^+} & \overset{pK}{\rightleftharpoons} & \mathrm{AH^+} \end{array}$$

also leads to

$$E_{1/2}(\mathrm{AH/AH^+}) - E_{1/2}(\mathrm{A^-/A}) = 2.3RT(pK_R - pK); \quad (53)$$

we finally have

$$\Delta\Delta G = 2.3RT(pK_R - pK^*). \quad (54)$$

Thus it follows from Eqn.(54) that the increase of the rate constant for the quenching of the excited state of the protonated acceptor molecules by the electron donor molecules is determined by the condition $pK_R > pK^*$. For the photochemical reduction of Thionine by aromatic hydrocarbons[57], the Thionine triplet state quenching constant is higher in an acid medium, which is consistent with the conclusion which follows from Eqn.(54), since $pK_R = 10.4$ and $pK^* = 7.0$ for Thionine.

At the same time, according to Eqns.(44) and (45), the rate constant for electron transfer within the collision complex can be expressed in terms of the changes in the free energy of activation. In the case of an endothermic electron transfer reaction the ratio of the electron transfer rate constant for the reactions of protonated ($k^a_{30,40}$) and deprotonated ($k^b_{30,40}$) excited molecules can be expressed in terms of pK_R and pK^* in the following way:

$$\ln\frac{k^a_{30,40}}{k^b_{30,40}} = 2.3(pK_R - pK^*). \quad (55)$$

Consequently a conclusion concerning the comparative reactivities of the protonated and deprotonated excited molecules can be based on the values of pK_R and pK^*.

2. Relation between the Reactivity and the Nature of the Electronic Excitation

For photochemical electron transfer reactions, the excited electronic n,π^* and π,π^* states are of greater interest. The n,π^* state is populated as a result of the $n \to \pi^*$ transition in which the n electrons of the heteroatom pass to the antibonding π orbital. The maximum information about the involvement of the T_{n,π^*} states in photochemical reactions has been obtained in relation to carbonyl compounds[34,138,139]. The high reactivity of the T_{n,π^*} states in the electron transfer reaction is due to the appearance of an electron density deficit at the oxygen atom of the carbonyl group as a result of the $n \to \pi^*$ transition. Thus the photochemical reduction of benzophenone and acetophenone in aqueous solutions as a result of electron transfer from a carbonate ion has been investigated[140].

A high reactivity of triplet n,π^* states has been observed also for aromatic quinones (benzo-, naphtho-, and anthra-quinones) with the lowest T_{n,π^*} level. A number of studies have been made[140–146] in which semiquinone radicals were formed as a result of electron transfer from a series of inorganic anions (CO_3^{2-}, SO_4^{2-}, Cl^-, SCN^-, PO_4^{3-}, OH^-, etc.). Quantitative measurements of the electron transfer rate constant in photochemical reduction reactions have been made for anthraquinones in aqueous solutions[145,147,148] by the method of competition kinetics. The rate constants for electron transfer to the T_{n,π^*} state of anthraquinone-2,6-disulphonic acid are 1.8×10^6 litre $mol^{-1}\ s^{-1}$ for HCO_3^- and 7.1×10^6 litre $mol^{-1}\ s^{-1}$ for OH^-.

As shown above, the rate constant for electron transfer in the collision complex is a measure of the reactivity of the excited state, but it can be by no means always determined or estimated. The quantum yield of the electron transfer products γ can also serve as a relative measure of reactivity. Measurements have been made[140] of γ for the formation of $CO_3^{\dot{-}}$ in the photochemical oxidation of carbonate by different quinone derivatives. It follows from the results of this study that naphtho- and anthra-quinones can be separated into two groups: those which oxidise carbonate with a quantum yield γ close to unity (1,4-naphthoquinone, 8-methyl-1,4-naphthoquinone, and anthraquinonesulphonic acid) and those which do not oxidise carbonate ($\gamma < 10^{-3}$; hydroxy- and amino-derivatives of naphtho- and anthraquinones).

This difference between reactivities can be associated with the different positions of the triplet n,π^* and π,π^* levels in the anthraquinone molecules[149,150]. The much lower reactivity of the triplet π,π^* states compared with the n,π^* states of aromatic carbonyl compounds is associated with the absence of a deficiency of electron density at the oxygen atom of the carbonyl group. The lack of data for the electron transfer rate constants involving carbonyl T_{π,π^*} states hinders a quantitative estimate of the reactivity of such states. The principal conclusions on this subject have been reached by comparing the yields γ of the products of the photochemical reduction of carbonyl compounds with different positions of the triplet n,π^* and π,π^* levels.

Despite the considerable differences between the reactivities of the T_{n,π^*} and T_{π,π^*} states, it has been noted that the acetophenone derivatives, which have a lowest T_{π,π^*} level, are capable of photochemical reduction with an appreciable yield[151,152]. For the alkyl phenyl ketones investigated, it is known that (a) $\Delta E \cong 1000\ cm^{-1}$ and (b) the wave function of the T_{π,π^*} state becomes "mixed" with that of the T_{n,π^*} state. Thus the photochemical reduction of phenyl ketones proceeds via a lowest triplet π,π^* state, which has partial n,π^* character and which is responsible for the appreciable quantum yield of the reaction. The reaction can also proceed via a highest T_{n,π^*} state (with a lowest T_{π,π^*} state) populated on thermal excitation[153].

Thus, examination of the data presented reveals a significant difference between the reactivities of the molecules of carbonyl compounds and quinones in the T_{n,π^*} state (compared with T_{π,π^*}) in the electron transfer reaction.

VI. THE INTERMEDIATE STATES IN THE FORMATION OF RADICAL-IONS

As stated above, solvated radical-ions are formed in the photochemical electron transfer reaction between the donor and acceptor molecules via a series of intermediate states including the exciplex and the solvate-separated radical-ion pair. The exciplex or the complex in the excited state are formed as a result of the interaction of the excited (singlet, triplet) donor (acceptor) molecule with a non-excited acceptor (donor) molecule[154-158]. The formation of an exciplex has been observed in non-polar (weakly polar) media on the basis of the appearance of a structureless luminescence band or of a transient absorption[159,160]. The existence of singlet exciplexes has been established reliably for atomatic hydrocarbons[48,161-171], aminopyridine[172], fluorene[173], transition metal complexes[174], etc. Triplet exciplexes have been investigated in less detail, mainly due to the extremely low phosphorescence quantum yields in the liquid solutions. The existance of triplet exciplexes is therefore established on the basis of the appearance of a transient absorption. The formation of triplet exciplexes has been observed between metalloporphyrins and aromatic nitro-compounds[175-177], chlorophyll and *p*-benzoquinone[178], phaeophytin and *p*-benzoquinone[179], benzene (and its methyl derivatives) and tetracyanobenzene[180], etc. The formation of triplet exciplexes has also been postulated in a number of studies of the mechanism of the quenching of the triplet state of thiazine[94,95] and polymethine dyes[120].

Measurements of the absorption spectra of the exciplexes by the method of laser photolysis[160] showed that the exciplexes have in many instances the structure of an ion pair[164-167,181]. At the same time it also follows from spectroscopic and thermodynamic data that the triplet exciplexes of many metalloporphyrins in the chlorophyll have the structure of an ion pair with partial charge transfer[177,178]. The wave function of the exciplex can be represented by a combination of the wave functions of states with complete charge transfer and states with excitation localised at one of the components of the complex[61,182]:

$$\psi_{exc} = \alpha\psi_1(\bar{A}D^+) + \beta\psi_2(A^*D) + \gamma\psi_3(AD^*). \qquad (56)$$

For singlet exciplexes comprising aromatic hydrocarbons and amines and also heterocyclic compounds and amines, which have the ionic structure A^-D^+, measurements have been made of the dipole moments μ, the heats of formation ΔH, and the molecular volumes ΔV. Thus $\mu = 13.3 \pm 1.7$ D for the exciplex of 3,4-benzacridine and diethylaniline[170]. The heats of formation $-\Delta H$ vary from 6.6 to 10.2 kcal mol^{-1} on passing from the exciplex of biphenyl and diethylaniline to the exciplex of anthracene and diethylaniline[48]. The change in molecular volume on formation of the exciplex relative to the initial components is $-\Delta V = 15.5$ cm^3 litre mol^{-1} for the pyrene–diethylaniline pair[170].

As stated above, in contrast to charge-transfer complexes, exciplexes are formed only in the excited state and this leads to the quenching of the fluorescence of the initial molecules (for singlet exciplexes) or to the quenching of the triplet–triplet absorption (for triplet exciplexes) and is accompanied by the appearance of a new luminescence or transient absorption. The mechanism of the electron transfer reactions leading to the formation of an exciplex is in broad outline analogous to Scheme 1. The application of picosecond laser excitation made it possible to obtain a series of data on the kinetics of the formation of exciplexes[183-185]. It has been shown for the exciplex of anthracene and diethylaniline that the exciplex formation rate constant is equal to the diffusional constant $(10 \pm 1) \times 10^{10}$ litre mol^{-1} s^{-1}. The formation of an exciplex of anthracene and diethylaniline in pure diethylaniline is slower than in hexane, since the rate-limiting stage of the reaction is orientational relaxation whose period is longer in diethylaniline than in hexane.

In non-polar and weakly polar media the formation of solvated radical-ions is usually not observed and the excitation energy is degraded as a result of a set of radiative and non-radiative processes. The solvated radical-ions can be formed in non-polar media as a result of two-quantum reactions, in which the second quantum is absorbed by the exciplex[160]. The non-radiative processes occurring in singlet exciplexes can be represented by a set of the following reactions[186-188]:

$$^1A^* + D \rightleftharpoons (^1A^*D) \rightarrow {}^1(A^-D^+)_{fc}, \qquad (XII)$$

$$^1(A^-D^+)_{fc} \rightarrow {}^1(A^-D^+), \qquad (XIII)$$

$$^1(A^-D^+)_{fc} \rightarrow {}^3A^* + D, \qquad (XIV)$$

$$^1(A^-D^+) \rightarrow A + D + D)_{fl}, \qquad (XV)$$

$$^1(A^-D^+) \rightarrow {}^3A^* + D, \qquad (XVI)$$

$$^1(A^-D^+) \rightarrow {}^1[A^-D^+] \qquad (XVII)$$

$$^1[A^-D^+] \rightarrow A + D + h\nu_{fl}, \qquad (XVIII)$$

$$^1[A^-D^+) \rightarrow A + D. \qquad (XIX)$$

The electron transfer takes place in a collision complex and leads to the formation of a Franck–Condon state of the exciplex [reaction (XII)] which is followed by the vibrational relaxation process (XIII). When the exciplex passes to a thermalised state, a "fast" intercombination transition to the triplet state [reaction (XIV)] competes. The subsequent deactivation processes include fluorescence from a vibrationally relaxed state [reaction (XV)], a "slow" intercombination transition to triplet states [reaction (XVI)], and a transition to a fully relaxed state as a result of the reorientation of the solvent molecule [reaction (XVII)], which is followed by fluorescence [reaction (XVIII)] and recombination [reaction (XIX)] processes. According to a series of data[163-165,189], the ratio of the rate constant for the radiative deactivation of the exciplex to the overall rate constant for the non-radiative deactivation process is in the range 0.01 to 1.5 for the perylene–dimethylaniline, 1,12-benzoperylene–*p*-chloro-*N*,*N*-dimethylaniline, etc. complexes.

In polar media the lifetime of the exciplex is shortened and this is accompanied by a decrease of the fluorescence yield and the appearance of solvated radical-ions. It has been shown[190] for the exciplex of anthracene and diethylaniline that the solvate radical-ions can be formed via the exciplex. According to a study[191] by the method of laser photolysis, an increase in the dielectric constant of the medium alters the electronic structure of the exciplex.

In weakly polar and polar media a solvate-separated radical-ion pair is an intermediate in the formation of solvated radical-ions. The formation of a solvate-separated radical-ion pair was demonstrated[192] on the basis of absorption spectra measured 50 ns after the laser excitation of pyrene in the presence of an electron acceptor–dicyanobenzene in dichloromethane. Parallel photoconductivity measurements demonstrated the absence of solvated radical-ions in the course of 50 ns after photoexcitation.

The processes occurring in the singlet radical-ion pairs can be represented by the following reactions:

$$^1A^* + D \rightleftharpoons (^1A^*D) \rightarrow {}^1(A^{\ddagger} \ldots D^{\ddagger}), \qquad (XX)$$

$$^1(A^{\ddagger} \ldots D^{\ddagger}) \rightarrow A + D, \qquad (XXI)$$

$$^1(A^{\ddagger} \ldots D^{\ddagger}) \rightarrow {}^3(A^{\ddagger} \ldots D^{\ddagger}), \qquad (XXII)$$

$$^1(A^{\ddagger} \ldots D^{\ddagger}) \rightarrow {}^1[A^{\ddagger} \ldots D^{\ddagger}], \qquad (XXIII)$$

$$^1[A^{\ddagger} \ldots D^{\ddagger}] \rightleftharpoons A^{\ddagger} + D^{\ddagger}. \qquad (XXIV)$$

The electron transfer takes place in the collision complex and leads to the formation of a "primary" radical-ion pair $^1(A^{\bar{\cdot}}...D^{+\cdot})$ [reaction (XX)], which is apparently similar to the Franck–Condon state of the exciplex[193]. The dissociation of the solvate-separated radical-ion pair $^1[A^{\bar{\cdot}}...D^{+\cdot}]$ into solvated radical-ions [reaction (XXIV)] precedes the recombination [reaction (XXI)] and intercombination conversion [reaction (XXII)] processes and the orientational relaxation of the solvent [reaction (XXIII)] in the pair $^1(A^{\bar{\cdot}}...D^{+\cdot})$.[193–195]. According to a number of studies[195–197], the recombination process takes place over a period of ~10 ns. The intercombination transition can be extremely effective as a consequence of the interaction between the electron spins and nuclei and can take place over a period of several nanoseconds[197–199].

The processes in triplet radical-ion pairs are fundamentally analogous to the processes in the singlet pairs. The main difference consists in the times of the recombination processes. Thus according to Gouterman and Holten[77], the recombination time in the singlet radical-ion pair formed by bacteriophaeophytin and *p*-benzoquinone is 5 ps, while the recombination time in the triplet pair is significantly greater than 230 ps. The difference between the recombination times is responsible for the difference between the quantum yields in the formation of solvated radical-ions via the excited singlet and triplet states.

VII. THE ROLE OF THE MEDIUM IN ELECTRON TRANSFER PROCESSES

As mentioned above, solvated radical-ions are formed as the final electron transfer products in photochemical reactions only in polar media, which has been manifested experimentally by the transient absorption of the radical-ions or the transient conductivity of the solution. In non-polar media there is no photoinduced absorption or photoinduced conductivity. Studies of the electron transfer mechanism[25,69–71] in media of different polarity have demonstrated the relation between the intermediate states in electron transfer. Scheme 7 presents the fundamental processes in the photochemical oxidation of a donor $^{1,3}D^*$:

Scheme 7

$$^{1,3}D^* + A \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} (^{1,3}D^*A) \begin{cases} \overset{k_{23}}{\underset{k_{32}}{\rightleftharpoons}} {}^{1,3}[D^+A^-] \\ \overset{k_{34}}{\underset{k_{43}}{\rightleftharpoons}} {}^{1,3}[D^{+\cdot}...A^{\bar{\cdot}}] \overset{k_{56}}{\underset{k_{65}}{\rightleftharpoons}} D^{+\cdot} + A^{\bar{\cdot}} \end{cases} \qquad k_{45} \downarrow \uparrow k_{54}$$

The pathway followed in the electron transfer reaction can be traced from the changes in free energy as a function of the dielectric constant of the medium[200]. The change in the free energy of formation of the exciplex ΔG_{23} (notation of Scheme 7) is given by the following expression according to Eqns.(14) and (15) and Knibbe[48]:

$$\Delta G_{23} = \Delta G_{23}(\text{hexane}) - \frac{\mu^2}{r^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1} - 0.186\right). \qquad (57)$$

The change in the free energy of formation of the solvate-separated radical-ion pair ΔG_{34} is given by the following equation according to Eqns.(14)–(16):

$$\Delta G_{34} = [E_{1/2}(D/D^+) - E_{1/2}(A^-/A)]_{\varepsilon_0} - \frac{e^2}{\varepsilon a} + \Delta G_{\text{solv}} - E(^1,^3D^*), \qquad (58)$$

where

$$\Delta G_{\text{solv}} = \frac{e^2}{2}\left(\frac{1}{R_{D^+}} + \frac{1}{R_{A^-}}\right)\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_0}\right) \qquad (59)$$

is the change in the free energy of solvation on passing from a medium with a dielectric constant ε_0 (in which the polarographic oxidation-reduction potentials are measured) to a medium with a dielectric constant ε. The change in the free energy of formation of solvated radical-ions $\Delta G_{34} + \Delta G_{56}$ is described by an expression analogous to Eqn.(10).

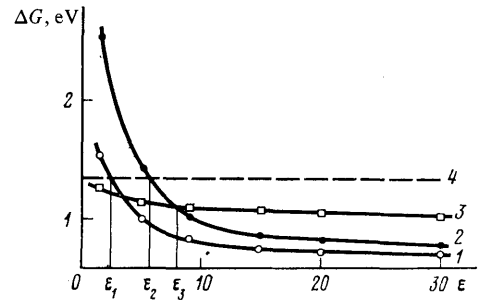


Figure 4. Dependence of the change in the free energy ΔG of formation of a solvate-separated radical-ion pair (curve *1*), solvated radical-ions (curve *2*), and the exciplex (curve *3*) for the chlorophyll *a*–*p*-benzoquinone system on the dielectric constant of the medium ε; curve *4* represents the position of the triplet level of chlorophyll *a*.[201]

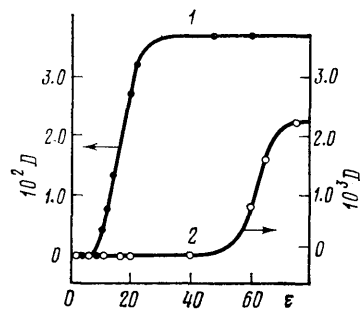


Figure 5. Dependence of the optical density *D* of the chlorophyll *a* radical-cation on the dielectric constant of the medium in the presence of *p*-benzoquinone (curve *1*) and nitrobenzene (curve *2*).[202]

Fig.4 presents the variation of the changes in the free energies of formation of the exciplex, the radical-ion pair, and solvated radical-ions based on the data of Andreeva and Chibisov[201]. Examination of the relations in Fig.4 shows, firstly, that in non-polar media the values of ΔG_{34} and $\Delta G_{34} + \Delta G_{56}$ are significantly positive in relation to the donor excitation energy, while ΔG_{23} is negative. This explains the possibility of the formation of the exciplex alone and hence the absence of solvated radical-ions. Secondly, with increase of ε for the medium, both ΔG_{34} and $\Delta G_{34} + \Delta G_{56}$ decrease, changing sign at dielectric constants ε_1 and ε_2 respectively. Consequently radical-ions are formed when $\varepsilon > \varepsilon_2$. Thirdly, ΔG_{34} becomes more negative than ΔG_{23} when $\varepsilon > \varepsilon_3$, as a consequence of which the radical-ion pair is formed effectively directly via the collision complex.

The results of the study of the dependence of the yield of the radical-ions on ε for the medium have shown that it is described by an S-shaped curve[202,203]. This type of relation can be understood by referring to Figs.5 and 6. At low dielectric constants of the medium the yield of radical-ions is virtually zero owing to the energetically unfavourable electron transfer process in the collision complex and also the necessity to overcome the Coulombic interaction forces in the radical-ion pair when the latter dissociates into radical-ions. With increase in the dielectric constant of the medium, a monotonic increase of the concentration of radical-ions to a maximum is observed. For higher values of ε, the free energies $\Delta G'$ and $\Delta G''$ become significantly negative; furthermore, the energy of the Coulombic interaction in the ion pair diminishes, which significantly facilitates its dissociation into solvated radical-ions.

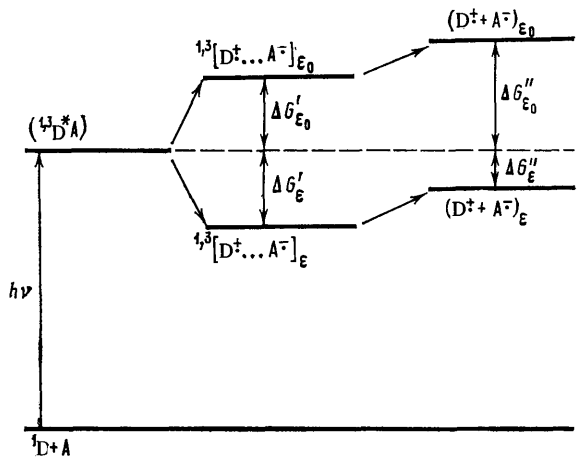


Figure 6. Schematic illustration of the arrangement of the energy levels of the intermediate states for low (ε_0) and high (ε) dielectric constants of the medium.

A quantitative expression for the dependence of the quantum yield in the formation of radical-ions on the dielectric constant of the medium can be obtained as follows. It is assumed that the quenching of the fluorescence of the acceptor by the electron donor can be neglected. It then follows from Eqn.(35) that

$$\varphi_{A^{\mp},D^{\pm}} = \varphi_T\left(\frac{k_{60}}{k_{60}+k_{65}}\right)\left(\frac{k_q^T\tau_T^0[D]}{1+k_q^T\tau_T^0[D]}\right). \qquad (60)$$

The dependence of $\phi_{A^{\mp},D^{\pm}}$ on ε is determined by the relations $k_{60}(\varepsilon)$ and $k_q^T(\varepsilon)$. The expression for $k_{60}(\varepsilon)$ assumes the form[203]

$$k_{60}(\varepsilon) = \frac{\text{const}}{\eta\varepsilon^{3/2}}\exp\left(-\frac{e^2}{\varepsilon aRT}\right), \qquad (61)$$

where η is the solvent viscosity.

The dependence of k_q^T on ε is determined, according to Eqn.(36), by the quantities $k_{40}(\varepsilon)$, $k_{41}(\varepsilon)$, and $k_{60}(\varepsilon)$. In the case where $\Delta G_{40} \ll 0$ (Scheme 2) the quenching rate constant $k_q^T(\varepsilon)$ can be expressed in a form analogous to that of Eqn.(23):

$$k_q^T(\varepsilon) = k_{34}/[1 + k_{43}/(k_{65} + k_{60}(\varepsilon))]. \qquad (62)$$

In the case where $\Delta G_{40} > 0$ the expression for $k_q^T(\varepsilon)$ is analogous to Eqn.(24):

$$k_q^T(\varepsilon) = \frac{k_{34}(k_{65}+k_{60}(\varepsilon))}{2k_{43}}\exp\left(-\frac{\Delta G_{40}(\varepsilon)}{RT}\right), \qquad (63)$$

while the expression for $\Delta G_{40}(\varepsilon)$ is analogous to Eqn.(58).

The formation of intermediates in electron transfer and their subsequent transformations depend significantly on the ratios of the excitation energies of one of the reactants, the electrochemical oxidation-reduction potentials, and the dielectric constant of the medium. By varying these parameters, it is possible to alter the efficiency of the formation of intermediates in the electron transfer reaction.

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Thermal Decomposition of Lanthanide, Yttrium, and Scandium Oxalates and Carbonates

V.A.Sharov and G.V.Bezdenezhnykh

Data concerning the thermal decomposition of lanthanide, yttrium, and scandium oxalates and carbonates are surveyed. The complexity of the process, the large number of stages involved, and the dependence of the composition of the intermediates in the thermal transformations on the experimental conditions is noted. Certain process characteristics have been discovered and it is concluded that the decomposition process depends on the ionic radius of the metal. The bibliography includes 83 references.

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I. INTRODUCTION

In the review an attempt is made to survey the existing data on the thermal decomposition of lanthanide, yttrium, and scandium oxalates and carbonates. The principal studies in this field have been carried out in the last 2–3 decades.

In the thermal decomposition of hydrated lanthanide oxalates it is possible to distinguish two stages: dehydration and decomposition of anhydrous oxalates. The available literature data for each stage are not unambiguous due to the dependence of the results on the experimental conditions (the rate of heating, the size of the specimen sample, the sensitivity of the apparatus, etc.). From a critical examination of the available data, we have attempted to reach certain conclusions about the compositions of the intermediate hydrates and about the changes in the nature and strength of the bonds in the series of compounds considered.

II. DEHYDRATION OF OXALATES

The dehydration of lanthanide oxalates proceeds with formation of intermediate hydrates. The dehydration process has been investigated by derivatographic methods in various media (air, argon, and CO_2) and *in vacuo* and also by infrared spectrophotometry and diffractometry.

In the first studies[1,2] of the dehydration of lanthanide oxalates at heating rates of 6, 2.5, and 0.33 K min^{-1} it was already observed that the composition and the region of stability of the intermediate hydrates depend on the heating rate of the specimen, the size of the sample, and the sensitivity of the apparatus. Systematic treatment of the result of subsequent studies confirmed this conclusion[3–27]. In this connection studies of the dehydration of all the lanthanide oxalates under the same conditions are of greatest interest for the elucidation of the characteristics of the dehydration process.

The first attempt to subdivide all the lanthanide oxalates into groups based on their ability to form intermediate hydrates of definite composition was made by Wendlandt[4,28]. He assigned to the first group lanthanum, praseodymium, and neodymium oxalates, for which the formation of intermediate hydrates has not been observed: the decahydrates decompose to the anhydrous compounds. For the oxalates of the second group (Sm–Dy) for formation of various hydrates and anhydrous oxalates has been observed. The oxalates of the third group (Y, Sc, Ho–Lu) give rise to stable dihydrates. Cerium oxalate does not belong to any of these groups.

Möbius and Matthes[7,8] divided the hydrated oxalates into three groups on the basis of very careful investigations. The thermogravimetric (TGA) and differential thermographic (DTA) curves for the decomposition of the oxalates of the first group (La, Ce, Pr) do not indicate the formation of lower hydrates. The oxalates of the second group (Sm–Tb) split off water in three stages, forming hexahydrates, 3,5-water oxalates, and anhydrous oxalates. Water is given up by the oxalates of the third group (Y, Er, Lu) in two stages with formation of trihydrates and dihydrates without any sign of the formation of anhydrous oxalates. Neodymium and holmium oxalates constitute transitions between two groups, while dysprosium oxalate does not form part of any of the above groups. The authors carried out their investigations at heating rates of 2, 1.1, 0.7, and 0.48 K min^{-1} and also by the isothermal heating method. In all cases decrease of the heating rate made it possible to discover the intermediates more effectively. For example, decrease of the rate of heating of the oxalate nonahydrate from 2 to 0.6 K min^{-1} showed that a relatively unstable trihydrate is formed in addition to the stable dihydrate.

The dependence of the dehydration process on the specimen sample size at a heating rate of 5 K min^{-1} has been investigated[24] for the yttrium compound. For a 500 mg sample, the curve describing the dehydration of yttrium oxalate has a single maximum, for a 318 mg sample it has three maxima, and for a 13.3 mg sample it has five maxima; the compositions of the intermediates are also correspondingly different.

Thus the temperatures of the formation and the temperature ranges corresponding to the existence of the hydrates cannot be regarded as definite constant quantities.

Data concerning the possibility of obtaining anhydrous oxalates in air are also contradictory[7,11,12,16,18,19]. On the other hand, investigators agree unanimously that *in vacuo* complete dehydration of the oxalate hydrates is attained[13,29–31].

Whereas much attention has been devoted in the literature to the composition of the intermediate hydrates of rare earth oxalates, no conclusions have been reached on the basis of the stepwise elimination of water. For example, it has been

shown clearly[2,4] that the number of dehydration stages increases in the oxalates of the elements ranging from lanthanum to dysprosium. According to these authors, this is because with increase of the atomic number of the element, the strength of the hydrogen and coordinate bonds involving the water molecules in the rare earth oxalate hydrates changes. In other words the activation energies for the elimination of water molecules linked by hydrogen (E_h^a) and coordinate (E_c^a) bonds are approximately the same for hydrated lanthanum oxalate, while $E_h^a < E_c^a$ for dysprosium oxalate.

It is also known[7,8,25,32-35] that the oxalate decahydrates of the elements located at the beginning of the series (La–Nd) lose the entire outer-sphere water and most of the coordinate water in a single stage, while closer to the centre of the series (Sm–Tb) only the outer-sphere water is lost and at the end of the series the outer-sphere and approximately half of the inner-sphere water is lost (in a single stage) (Fig.1).

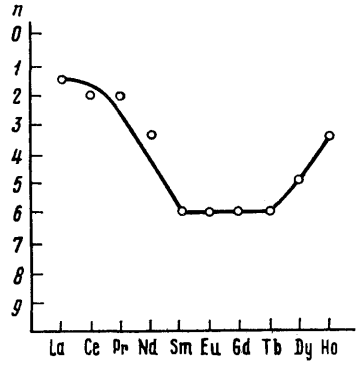


Figure 1. The first stage of the transition $Ln_2(C_2O_4)_3 \cdot 10H_2O \rightarrow Ln_2(C_2O_4)_3 \cdot nH_2O$ on heating. The curve has been plotted on the basis of the data of Bezdenezhnykh et al.[24,32]

It follows from Fig.1 that, on passing from La and Ce to Sm in the series of lanthanide oxalates, the strength of the bond between the lanthanide and the coordinated water increases; on passing from Sm to Tb, the bond strength hardly changes and subsequently weakens. There is not yet a molecular orbital scheme for the σ-bonds of complexes with a central ion having a coordination number of eight or nine. It is known only that the covalent bond between the rare earth ions and ligands is formed mainly as a result of the mixing of the occupied ligand orbitals with the partly filled 4*f* orbitals and the vacant 6*s*, 6*p*, and 5*d* orbitals of the rare earth ions[36]. An admixture of covalent character in an ionic bond should favour the formation of coordination polyhedra with vertices pointing in the directions of the maxima of the hybrid sp^3d^n orbital. This requirement is satisfied in the first place by the 9-coordination polyhedron with D_{3h} symmetry. For polyhedra with a coordination number of 8, the dodecahedron with D_{2d} symmetry is most preferred. However, the ionic contribution is greater than the covalent contribution[37].

It is interesting that the nature of the variation of the Ln-coordinated water bond strength in the rare earth oxalate decahydrates is the same as that of the variation of the stability of the octahedral complexes in the series of rare earths[38]. This justifies the hypothesis that the arrangement of the molecular orbitals (bonding, non-bonding, and the first antibonding) in polyhedra with coordination numbers of 6 and 9 is the same, the difference consisting in the number of lowest bonding orbitals (6 for an octahedron and 9 for a 9-coordination polyhedron), which are localised mainly at the ligands[38,39].

Using this orbital scheme, it is possible to explain the variation of the lanthanide-coordinated water bond strength in the series of lanthanide oxalate decahydrates (Fig.1). The increase in the strength of the Ln–H_2O bond on passing from Pm to Ce, Pr, Nd, and Sm is due to the enhancement of the bonding effect, which is determined by the possible increase of the overlap integrals (decrease of the Ln–H_2O distance) and the increase of the ionisation potential. On passing from Pm to Sm–Gd, the increase of the stability of the compounds slows down (or even ceases) because electrons appear in the antibonding t_{1u}^* orbital[38]. Beyond Tb, the Ln–H_2O bond weakens, since electrons fill the t_{1u}^* orbital.

The coordinated water in Nd–Er oxalates is split off stepwise. Its elimination temperature increases up to Tb–Dy and then falls (Fig.2), which is consistent with the above considerations concerning the nature of the variation of the Ln–H_2O (coordinated) bond strength.

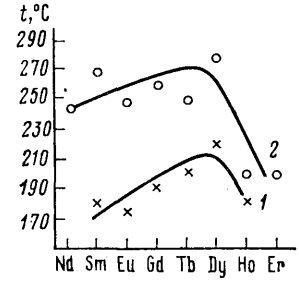


Figure 2. The minima on the DTA curves for the decomposition of the lanthanide oxalates corresponding to the loss of coordinated water: 1) first stage; 2) second stage[28].

The dehydration of terbium, ytterbium, and lutetium oxalate hexahydrates proceeds isotypically in two stages with formation of the relatively unstable trihydrate and the dihydrate, which is stable in the temperature range 200° to 350 °C.[7,8,24] It is therefore difficult to discover how the Ln–H_2O (coordinated) bond strength varies from Tm to Lu. Theoretically it should decrease, since the filling of antibonding orbitals with electrons is characteristic of Tm, Yb, and Lu.[38,39]

III. DECOMPOSITION OF OXALATES AFTER DEHYDRATION

In the study of the decomposition of rare earth, yttrium, and scandium oxalates in air, different workers obtained compounds having the following compositions:

$Ln_2(C_2O_4)_3$ 2, 11, 17, 23, 40 — 42 ; $Ln_2(C_2O_4)_2O$ 29 ;
LnC_2O_4 42 ; $Ln_2O_2(C_2O_4)_2$ 9,18 ; $Ln_2O_2OCOCO_2$ 23 ;
$Ln(CO_3)_2C_2O_4$ 22, 43 ; $Ln(CO_3)_2O$ 29 ; $(LnCO_3)_2O$ 22, 42 ;
$Ln_2(CO_3)_2$ 2, 17, 41, 44 ; $Ln_2O_3 \cdot 2CO_2$ 2, 14, 39, 41
$Ln_2O_3 \cdot CO_2$ 1, 2, 4, 9 — 12, 14,24, 40 — 42 ; $(LnO_2)CO_3$ 14, 15, 18, 22, 23, 29 ;
$2Ln_2O_3 \cdot CO_2$ 2, 17, 18 .

Apart from the products quoted, CO, CO_2, and free carbon are liberated in the thermolytic process. The formation of carbon was noted for lanthanum[5,9,14,15,42], cerium[14], praseodymium[9,45], neodymium[2,9,45,46], samarium, gadolinium[45], terbium[24], dysprosium, erbium[45], and yttrium[2,24] oxalates. Carbon was not found in the decomposition of cerium, scandium[2], erbium, thulium, ytterbium, and lutetium[24] oxalates.

The most stable intermediate proved to be the basic carbonate $Ln_2O_3.CO_2$. It has been established in recent years by X-ray diffraction[45,57] that the composition of this compound is $Ln_2O_2.CO_3$ and that it should be most correctly referred to as the dioxomonocarbonate. In the thermolysis of thulium, ytterbium, and lutetium oxalates, $Ln_2O_2.xCO_3$ ($x < 1$), which is a mixture of the dioxomonocarbonate and the oxide Ln_2O_3, was found as an intermediate[47].

The presence of three polymorphic forms of the dioxomonocarbonates $Ln_2O_2.CO_3$, namely (I), (Ia), and (II), has been demonstrated[45] on the basis of high-temperature X-ray diffraction and density data, TGA curves, and infrared spectra. They were obtained in the decomposition of the following oxalates:

La	Pr	Nd	Sm	Eu	Gd	Structure
(I)	(I)	(I)	(I)	(I)	(I)	tetragonal
	(Ia)	(Ia)				monoclinic
(II)	(II)	(II)	(II)		(II)	hexagonal

These are layer type structures made up of planar $(Ln_2O_2)_n^{+}$ polymers and CO_3^{2+} groups. Form (I) has square layers, as in LnOCl and related compounds, while form (II) is characterised by hexagonal $(Ln_2O_2)_n^{2+}$ layers, as in the A-forms of sesquioxides.

In all cases form (I) is formed in the first place from $Ln_2(CO_3)_3$. The transformation of form (I) into form (II) is observed above 400 °C without weight loss. There is no definite evidence for the formation of form (II) for heavy lanthanides. It is interesting that an analogous behaviour has been observed for the oxides of light lanthanides; the conversion of the C form (cubic) into the A form (hexagonal) requires an increase of temperature, while for the heavy lanthanides only the C form has been discovered. Since the carbonate of form (II) can be regarded as layers of the A form of Ln_2O_3 separated by C–O layers, the tendency towards the transition form (I) (tetragonal) → form (II) (hexagonal) as a function of temperature and the probable absence of form (II) for the heavy lanthanides are apparently caused directly by the known tendency towards the existence of polymorphic regions in Ln_2O_3.

By analogy with the irreversible transformation of the C form of the oxide into the A form, the transformation of form (I) into form (II) is not reversible. Nevertheless the rate of this transformation is evidently greatly influenced by the presence of carbon and (or) the particle size. The data presented by the authors[11,18,20,26,47,62,63] suggest that form (I) is characteristic of all the lanthanides: the corresponding compounds of the heavy lanthanides decompose at temperatures only slightly above the temperatures at which they are obtained from $Ln_2(CO_3)_3$.[45]

On the basis of their own studies, the authors[47] explained the available TGA curves in the literature for the decomposition of lanthanide oxalates and carbonates. Depending on which lanthanide is investigated, three types of generalised curves are obtained. For La and Pr at a heating rate of 0.6 K h^{-1}, there is a phase change to $Ln_2O_2.CO_3$ (II). The latter is formed before the dissociation temperature is attained. For Nd and Sm–Gd at a heating rate of 0.6 K h^{-1}, the phase transition from $Ln_2O_2.CO_3$ (I) or (Ia) to $Ln_2O_2.CO_3$ (II) does not reach completion, because the thermal decomposition of phases (I) and (Ia) to Ln_2O_3 begins. The length of the plateau on the TGA curves depends on the heating rate.

It is known[47] that the $Ln_2O_2.CO_3$ (II) phase is not encountered when the ionic radius of Ln^{3+} is smaller than for Gd^{3+}. The formation of the $Ln_2O_2.CO_3$ (I) or (Ia) phase is characteristic on heating Tb–Lu oxalates or carbonates. The $Tb_2O_2.CO_3$ (I) and (Ia) forms have a high thermal stability, while $Yb_2O_2.CO_3$ (I) and (Ia) begin to decompose immediately after formation.

The decomposition temperatures of $Ln_2O_2.CO_3$ have been published[45,48–50]. The Dy, Ho, Er, and Y dioxomonocarbonates have been obtained by a hydrothermal method and their X-ray diffraction patterns (the values of *h*, *k*, *l*, *d*, *I*) have been published[51].

The thermolysis has been studied by the DTA method[10,12,14,15,22,42,52,53], which is more sensitive to phase transitions than the TGA method. The decomposition of the hydrated La,[10,14,15,42,52] Nd, Sm–Gd,[52] Tb–Lu[24,54], Y,[10,24,52,54] and Sc [10] oxalates in the range 300–600 °C is accompanied by complex exothermic processes, which are a consequence of the decomposition of the oxalates and demonstrate the simultaneous occurrence of two reactions: the endothermic decomposition of the oxalate or carbonates of various compositions and an exothermic reaction involving the interaction of CO and O_2 with formation of CO_2 and the oxidation of free carbon[14,42,43,55]. This has been confirmed, firstly, by the fact that the total amount of the evolved gases is greater than the weight loss by the sample[10] and, secondly, by the observation that the decomposition of, for example, yttrium oxalate in a helium atmosphere[10] or of lanthanum oxalate in an argon atmosphere[23] is accompanied by endothermic effects. Above 600–700 °C, exothermic processes associated with the crystallisation of cryptocrystalline oxides[52] and the conversion of the metastable C form of the oxide into the B form[53] are observed for all the oxalates.

Since the decomposition temperatures of the anhydrous oxalates increase in the La–Lu series[28], an impression has been created that the Ln–C_2O_4 bond strength increases in this series. However, one should bear in mind here that the increase of the Ln–C_2O_4 bond strength entails a decrease of the thermal stability of the oxygen-containing salts[57,58]. Hence it follows that the Ln–C_2O_4 bond strength should be weakened in the La–Lu series, which is consistent with the weakening of the basic properties in the same series. This weakening occurs monotonically from La to Tb, but subsequently, from Tb to Lu, the Ln–C_2O_4 bond strength hardly changes. Thus the nature of the variation of the Ln–C_2O_4 bond strength in the series of lanthanide oxalates differs from that for the Ln–H_2O bond strength. To a first approximation, this can be explained by the fact that, in contrast to the water molecules, the C_2O_4 groups can be linked to the central ion via not only σ-bonds but also via π-bonds.[59]

The final products of the decomposition of the oxalates are the oxides CeO_2, Pr_6O_{11}, Ln_2O_3 (Ln = La, Nd, Sm, Eu, Gd, Dy, or Ho), and Tb_6O_{11} (converted into $TbO_{1.714}$ with an endothermic effect at 865 °C).

The thermal dissociation reactions of the lanthanide oxalates *in vacuo* and in inert media proceed differently. The vacuum thermal decomposition of the La–Eu oxalates[44,60] takes place with formation of the intermediates $Ln_2(C_2O_4)(CO_3)_2$, $Ln_2(CO_3)_3$, $Ln_2O_{0.6}(CO_3)_{2.4}$, and $Ln_2O(CO_3)_2$, the evolution of CO and CO_2, and the formation of free carbon. All the oxides formed are black due to the presence of free carbon. Studies have been made of the oxalates of Ce,[9,13] La,[61] Nd–Sm, Gd–Dy, and Er,[20] Eu,[22,23,29,30] Yb,[27,29,43] Y,[26,62,63] and Sc.[3]

An attempt has been made[62] at a qualitative explanation of the formation of intermediates in the decomposition of *s*, *p*, and *d* metals as a result of the combination of various radicals formed on dissociation of $-M-C_2O_4-M-$ linkages, where M is a metal. Free carbon is obtained as a result of the disproportionation of CO or the decomposition of the carbon–oxygen polymers C_4O_3, C_8O_3, and $C_{12}O_9$, which have been described in the literature. These polymers can be obtained as a consequence of the combination of carbon–oxygen radicals formed on dissociation of the bonds in the C_2O_4 groups.

An attempt may be made to reach a series of conclusions from the data presented above.

1. Since the basic properties of the lanthanide ions weaken with increasing atomic number (with decreasing ionic radius), the strength of the bond formed between Ln^{3+} and the oxalato- or carbonato-group should decrease. This has been confirmed by the majority of investigations[2,11,31,45,48,61], with the exception of that of Palei et al.[17]

2. The weakening of the $Ln-CO_3$ bond with increasing atomic number of the lanthanide explains the preferential formation of the normal carbonates and compounds of the type $Ln_2O(CO_3)_2$ by the light lanthanides[2,14,15,41,60]. The carbonates of the heavy lanthanides are unstable and rapidly decompose to the oxides[31,45].

3. The mechanism of the thermal decomposition of light lanthanide oxalates should have the following general form:

$$\underset{\text{(III)}}{Ln_2(C_2O_4)_3} \rightarrow \underset{\text{(IV)}}{Ln_2(C_2O_4)_x(CO_3)_y} \rightarrow \underset{\text{(V)}}{Ln_2(CO_3)_3} \rightarrow \underset{\text{(VI)}}{Ln_2O(CO_3)_2} \rightarrow \underset{\text{(VII)}}{Ln_2O_2CO_3} \rightarrow \underset{\text{(VIII)}}{Ln_2O_3}$$

It is difficult to establish from available literature data how the values of x and y vary throughout the lanthanide series. According to general considerations, an increase of the atomic number of the lanthanide should entail an increase of x and a decrease of y. This has been confirmed by the finding that the degree of disproportionation of CO diminishes from Ce to Lu. However, the opposite conclusion can also be reached, because the relative amount of CO increases in the same direction.

As a consequence of the proximity of the decomposition temperatures of compounds (III)–(VI), it has not been possible to detect all five stages in the case of the heavy lanthanides *in vacuo*, in air, and in CO_2 and N_2 atmospheres. Here the mechanism is usually restricted to compounds (III), (VII), and (VIII). This is evidently also true of scandium and ytterbium oxalates.

4. The formation of $Ln_2O_2CO_3$ has been demonstrated by hydrothermal synthesis, X-ray diffraction analysis, infrared spectroscopy, and the discovery of three polymorphic forms. In order to confirm the variation of the above compounds in the series of lanthanides, additional studies are evidently necessary, because contradictory data have been published[47,48,51].

5. The decomposition of the lanthanide, yttrium, and scandium oxalates *in vacuo* and sometimes in air results in the formation of free carbon due to the disproportionation of CO or the decomposition of carbon–oxygen polymers[2,5,9,14,15,24,42,45,46]. The latter are obtained via the combination of the oxygen-carbon radicals arising after the dissociation of the bonds with the C_2O_4 group. According to various sources, carbon burns in air at a temperature in the range 460–680 °C.

6. In an inert atmosphere the thermal decomposition of the dehydrated oxalate is accompanied by endothermic effects. In air the exothermic effects associated with the oxidation of CO and C are superimposed on them.

7. Recently the majority of investigators have used the following terminology for the intermediates in the decomposition of the oxalates and carbonates; in $Ln_2O(CO_3)_2$—monoxodicarbonate; $Ln_2O_2.CO_3$ dioxomonocarbonate. The composition $Ln_2O_2.CO_3$ (and not $Ln_2O_3.CO_2$) has been confirmed by X-ray diffraction studies[45].

IV. THERMAL DECOMPOSITION OF CARBONATES

Data on the thermal decomposition of lanthanide carbonates represent additional information about the compositions and properties of lanthanide oxide carbonates. The decomposition of lanthanide and yttrium carbonates has been investigated[1,2,18,40,49,57,64–82].

The thermal stability of lanthanide carbonates increases with increasing atomic number of the metal[71]. Thus lanthanum carbonate begins to decompose at 495 °C, while erbium carbonate begins to decompose at 770 °C. In contrast to the oxalates, the decomposition of the carbonates of the light lanthanides[18] takes place only with formation of $Ln_2O_2.CO_3$; compounds of the type $2Ln_2O_3.CO_2$ are not formed. The decomposition of the carbonates of heavy lanthanides and yttrium[73] is accompanied by the formation of $Ln_2O_3.2CO_2$ and $Ln_2O_2.CO_3$. At temperatures of approximately 900 °C and above all the carbonates are converted into the oxides[75].

On the basis of literature data and the results of their own investigations, Kokhanovskii and Pavlyuchenko[82] concluded that the decomposition of lanthanide carbonates proceeds in accordance with the mechanism $Ln_2(CO_3)_3 \rightarrow Ln_2O_2.CO_3 \rightarrow Ln_2O_3$ and is accompanied by the formation of only one intermediate. At the same time, according to their data[82], it is possible to obtain the monoxodicarbonates $Ln_2O(CO_3)_2$. The latter was established from the slight inflections in the TGA and DTA curves. The existence of $Ln_2O(CO_3)_2$ could not be confirmed either by X-ray diffraction or by infrared spectroscopy. The thermal decomposition of dioxomonocarbonates should be an endothermic process. However, bearing in mind the crystallisation of both dioxomonocarbonates and oxides, it is to be expected that the endothermic effects will be significantly distorted by the superposition of the exothermic effects. In this respect the decomposition of yttrium and gadolinium carbonates is extremely characteristic, their thermograms showing only exothermic effects in the region of the decomposition of the dioxomonocarbonates[82].

The data presented on the thermal decomposition of lanthanide carbonates confirm the conclusions reached in the previous Section concerning the thermal stability and composition of and the sign of the thermal effect associated with the intermediates formed on heating anhydrous lanthanide oxalates (carbonates, dioxomonocarbonates). The individuality of $Ln_2O(CO_3)_2$ has not so far been confirmed experimentally.

V. KINETICS OF THE DEHYDRATION AND DECOMPOSITION OF LANTHANIDE OXALATES

There are literature data on the activation energies for the thermal decomposition of lanthanum[9,12,44,83], cerium[9,22], praseodymium[9], neodymium[9], and yttrium[22] oxalates. The enthalpies of the reaction $Ln_2O_3.CO_2 \rightarrow Ln_2O_3 + CO_2$ (where Ln = La, Nd, Sm, Gd, Dy, or Lu) have been calculated from DTA curves[65].

Evidently the kinetics of the dehydration of lanthanide oxalates and of the decomposition of the intermediates formed on heating the oxalates and carbonates have been very little investigated. The number of such studies is small and none

has dealt with the compounds of all the lanthanides. In the main there are data on the oxalates of the first half of the lanthanide group. However, despite the fact that the kinetic data are widely scattered, they permit certain conclusions: (1) the water in the hydrated oxalates is retained less strongly than the oxalato-group. In the range from lanthanum to neodymium the strength of the bond between the water molecules and the lanthanide ion increases[9]. (2) The strength of the bond formed by the carbonato-group in lanthanide dioxomonocarbonates diminishes in the sequence from lanthanum to lutetium[65].

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Ozonolysis—A Modern Method in the Chemistry of Olefins

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The review is devoted to the advances in the last ten years in the development of the ozonolysis of olefins as a synthetic method, in the study of the structures of peroxy-products of the azonolysis, and in the study of the stereochemistry of ozonides, which have in many respects determined the progress in our ideas concerning the mechanism of the ozonolysis of olefins.
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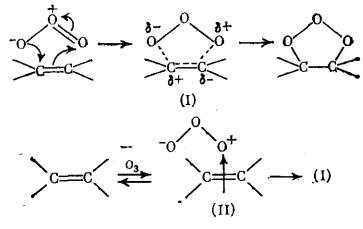
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I. INTRODUCTION

The ozonolysis† of olefins has become not only a recognised analytical method for the determination of the structures of unsaturated compounds, but also a method for the highly selective introduction of oxygen-containing functional groups into the organic molecule at the site of the double bond. The development of the ozone generation technique and of the ozonolysis process itself has attained a level such that this reaction has acquired increasing importance for technology[1]. In recent years the study of the structures of peroxy-products of ozonolysis and of the stereochemistry of ozonides, which has in many respects promoted progress in our ideas concerning the mechanism of the ozonisation of olefins, has been prosecuted particularly vigorously in recent years.

II. PEROXY-PRODUCTS OF OZONOLYSIS AND THE MECHANISM OF THE OZONISATION OF OLEFINS

It has now been established that the ozonolysis of olefins begins with the addition of an ozone molecule to the double bond. The adduct, in which the carbon–carbon bond still persists, has been called the primary ozonide[2] (in this review it is henceforth referred to as the primary ozonide). It is formed via a mechanism involving electrophilic 1,3-dipolar cycloaddition[3] via transition state (I) in which the electrophilic oxygen of the ozone molecule is bound to the carbon atom of the double bond more strongly than the nucleophilic oxygen atom. The interacting ozone and olefin molecules can attain the semipolar transition state (I) either via a single-step concerted cycloaddition[3] or via an additional reversible stage in which the π-complex (II) is formed[4-6]:



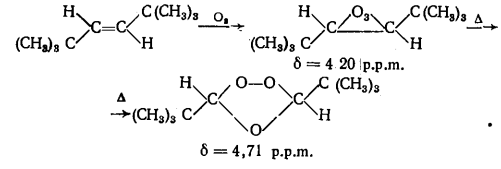
(I)

(II)

†The term "ozonolysis" is used in this review for the entire process involving the cleavage of the double bond by ozone, leading to the final peroxy- or non-peroxy-products. The term "ozonisation" refers only to the action of ozone on an unsaturated compound.

π-Complexes of ozone with aromatic compounds and arylethylenes have been detected by spectrophotometry and ^{1}H NMR at temperatures between −150 and −155 °C.[7,8] Similar complexes have also been observed for the usual olefins[9,10].

The formation of the primary ozonide is an irreversible process occurring with liberation of 37–39 kcal mol^{-1} of heat[11]. The primary ozonide derived from *trans*-1,2-di-t-butylethylene has been detected by ^{1}H NMR at −110 °C and its conversion into the normal ozonide with increase of temperature has been observed[12]:

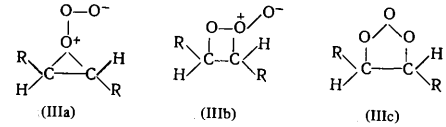


δ = 4.20 p.p.m.

δ = 4,71 p.p.m.

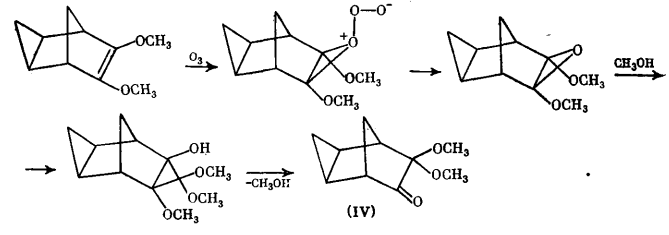
The primary ozonides of other olefins are less stable. The ^{1}H NMR spectra of the primary ozonides of *cis*-olefins recorded at −130 °C contain a broad and poorly resolved signal due to the ring protons in the range 4.35–4.40 p.p.m.[12,13] The greater stability of the primary ozonides derived from *trans*-olefins has been confirmed by quantum-mechanical calculations[14] and microwave spectroscopy[15].

Three probable structures of the primary ozonides have been discussed:



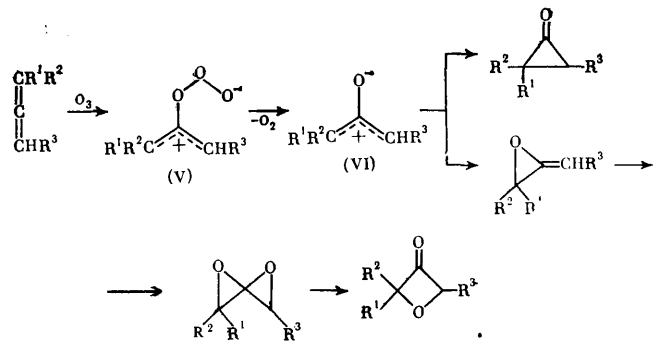
(IIIa) (IIIb) (IIIc)

The formation of the peroxyepoxide (IIIa) or the σ-complex can occur in the ozonisation of sterically hindered olefins, where the reaction products are epoxides[16-18]. The formation of the "anomalous" ozonolysis product (IV) has also been attributed to the formation of the σ-complex[19]:

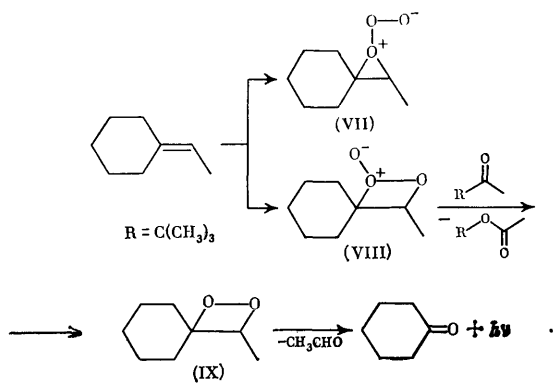


(IV)

In the case of hindered allenes the formation of the initial intermediate (V) as a consequence of the electrophilic attack by ozone has been postulated[20]. The elimination of oxygen leads to the stabilised zwitter-ion (VI), which is converted into the final ozonolysis products:



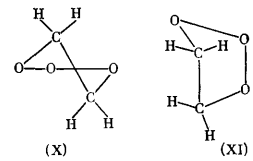
In conformity with the "unifying concept"[21], it has been suggested that the addition of ozone to the double bond of a compound, for example, ethylidenecyclohexane, gives rise to a peroxyepoxide or the σ-complex (VII), which is then converted into the Staudinger four-membered molozonide (VIII), capable of oxidising the excess aldehyde or ketone via a reaction of the Baeyer–Villiger type. The molozonide (VIII) is then converted into the dioxetan (IX) and then into cyclohexanone and acetaldehyde[22,23]:



However, these results were not subsequently confirmed[24–28].

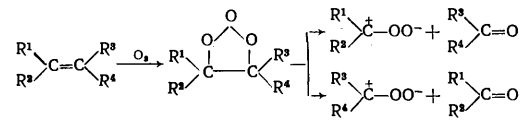
A decisive argument in support of the 1,2,3-trioxolan structure of the primary ozonide (IIIc) rather than that of the molozonide (IIIb) has come from ^{1}H NMR spectra[13,24]. Only one signal due to the methylidyne ring protons has been observed in the spectra of the primary ozonides of symmetrically disubstituted olefins, while in the case of structure (IIIb) these protons would not have been equivalent. Although in the peroxyepoxide (IIIa) both ring protons may also give rise to the same chemical shift, the signal would be significantly displaced downfield as a consequence of the deshielding influence of the positive charge on the neighbouring oxygen atom.

It has been suggested that the carbon–carbon bond in the 1,2,3-trioxolan ring has partial double bond character[29]. Indeed X-ray diffraction yielded a bond length of 1.44 Å, which is the mean of the lengths of single (1.54 Å) and double (1.34 Å) bonds[30]. The low stability of the primary ozonides hinders the study of their conformations by the usual methods. The quantum-chemical calculation, which permitted a choice between the possible half-chair (X) and envelope (XI) conformations of the primary ozonides of lower olefins in favour of the latter as the more stable, proved extremely effective[31]:

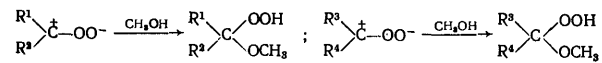


Thus electrophilic 1,3-dipolar cycloaddition of ozone to a carbon–carbon double bond results in the formation of a primary ozonide, which in most cases has the structure of a 1,2,3-trioxolan.

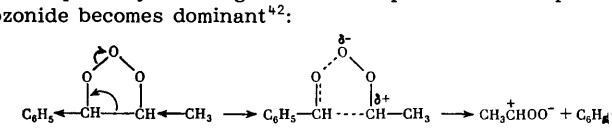
The energy-rich O–O–O linkage and the appreciable ring strain caused by the steric hindrance due to the three neighbouring oxygen atoms are responsible for the low stability of 1,2,3-trioxolan and the ease of its conversion into 1,2,4-trioxolan or the normal ozonide[32]. The mechanism of the conversion of the primary ozonide into 1,2,4-trioxolan has been widely discussed in the last ten years. Up to the middle of the 1960s, Criegee's mechanism[33], which provides a satisfactory explanation of the formation of normal and "cross" ozonides (both monomeric and oligomeric), cyclic dimeric and linear oligomeric peroxides, and "anomalous" ozonolysis products in ozonisation in inert solvents, as well as the formation of α-substituted hydroperoxides in ozonisation in a "participitating" proton-donating solvent of the type HX (X = OH, OR, OCOR, NH_2, NHR, NR_2 or CN), was generally accepted[16,34,35]. A fundamental feature of this mechanism is the formation of a zwitter-ion and of a carbonyl compound as a result of the heterolytic cleavage of the O–O and C–C bonds in the 1,2,3-trioxolan ring of the primary ozonide. For an asymmetric olefin, there is a possibility of two pathways leading to the cleavage of the primary ozonide with formation of different zwitter-ions:



It has been shown in many instances[11,36] that the mode of decomposition of the primary ozonide is determined mainly by the inductive effect of the substituents, while the mesomeric effect plays a secondary role[37]. The mode of the cleavage of primary ozonides can be conveniently investigated by analysing the products of the reaction of the zwitter-ions with methanol, which takes place quantitatively. The α-methoxyhydroperoxides formed correspond to the initial zwitter-ions[38–40]:

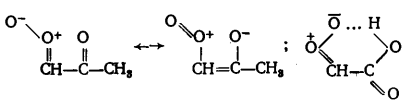


It has been established that electron-donating groups at the double bond promote the formation of a zwitter-ion with the neighbouring carbon atom as a consequence of the decrease of the local positive charge on the latter; correspondingly electron-accepting substituents destabilise the zwitter-ion and facilitate the formation of a carbonyl compound[39,41]. If the substituents exert the same influence, one of the pathways leading to the decomposition of the primary ozonide becomes dominant[42]:

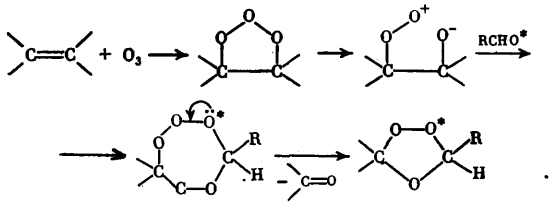


The groups stabilising the zwitter-ion can be arranged in the sequence $CH_3CO > CH_3COOH > C_6H_5 > H > CH_2OH > COOCH_3$. The stabilising influence of the keto-group can be accounted for by the possibility of its participation in the delocalisation

of the charge. The carboxy-group stabilises the zwitter-ion as a result of the formation of a hydrogen bond:

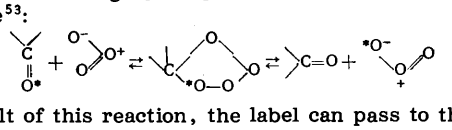


A pathway to the ozonide via a seven-membered cyclic intermediate (XII)—the product of the attack on the primary ozonide by an aldehyde molecule—which constitutes an alternative to the Criegee mechanism, has been proposed[43-46]. The main evidence in support of the new mechanism is the significant incorporation of the ^{18}O label into the peroxide bridge of the ozonide, which has been observed in the ozonisation of *trans*-1,2-di-isopropylethylene and ethylidenecyclohexane with participation of labelled acetaldehyde and propionaldehyde respectively[43,44]:

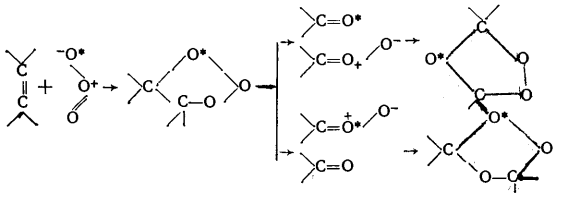


(XII)

The results of the ozonolysis of *cis*- and *trans*-di-isopropylethylenes in the presence of [^{18}O] isobutyraldehyde confirmed the preferential incorporation of the label in the peroxide bridge[47]. However, in the ozonisation of phenylethylenes in the presence of [^{18}O] benzaldehyde[42,48,49] and subsequently also of lower olefins (ethylene, propene, and *cis*- and *trans*-but-2-enes) in the presence of [^{18}O]formaldehyde or [^{18}O]acetaldehyde[50] the label was found exclusively in the ether position in the ozonides. Furthermore, the joint ozonolysis of *cis*- and *trans*-di-isopropylethylene in the presence of [^{18}O]acetaldehyde even at a very low temperature (−110 °C), i.e. under the most favourable conditions for the exchange reaction between the aldehyde and the primary ozonide[52] led to the incorporation of the label in the ether bridge to the extent of 90%. An attempt was made to explain the slight (approximately 10%) incorporation of the ^{18}O label in the peroxide bridge of the ozonide by postulating a reversible exchange [2 + 3] reaction between the aldehyde and ozone[53]:

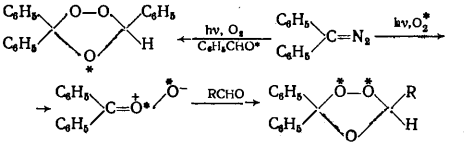


As a result of this reaction, the label can pass to the ozone molecule and with it into any position in the ozonide:

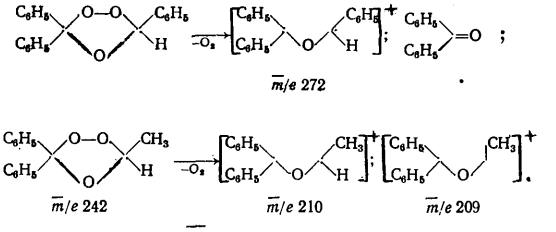


Although the possibility of such an exchange reaction of ozone with the aldehyde cannot be ruled out, under ozonisation conditions it can hardly compete appreciably with the very rapid reaction of ozone with the olefin.

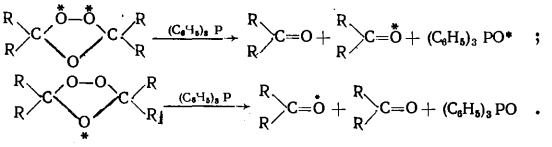
The conflict in the results for the distribution of the ^{18}O label in the ozonide can apparently be accounted for by differences in the methods of analysis. In some investigations[22,45,54] the ozonide was reduced with lithium tetrahydroaluminate with subsequent mass-spectrometric analysis of the resulting alcohols. In other investigations[42,47-49,51] the ozonides were subjected to a direct mass-spectrometric analysis. The method of microwave spectroscopy[15,50] is less susceptible to errors in interpretation, but it is applicable only to the ozonides of lower olefins. For ozonides known to contain the isotope label in the ether or peroxide position, it has been established that the M-32$^+$ fragment ion is formed as a result of the elimination of oxygen from the peroxide bridge of the ozonide. Such ozonides have been synthesised by the photoxidation of diphenyldiazomethane in the presence of benzaldehyde or acetaldehyde[55-58]:



The distribution of the label in ozonides is analysed by employing the molecular ion and the M-32$^+$ fragment[42,48,58]:



Labelled ozonides have been reduced with triphenylphosphine. Mass-spectrometric analysis of the resulting triphenylphosphine oxide showed that the attack is directed exclusively to the peroxide oxygen atom of the ozonide[58,59]:



This indirect method of determining the position of the ^{18}O label in ozonides proved to be the most reliable and convenient. With its aid it has been shown[58] that in the case of di-isopropyl ozonide—the product of the joint ozonolysis of di-isopropylethylene and ^{18}O-isobutyraldehyde—the label is located solely in the ether position, as shown by the absence of ^{18}O from triphenylphosphine oxide.

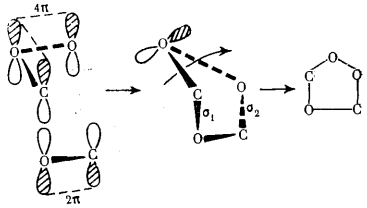
Thus the mechanism of the conversion of the primary ozonide into 1,2,4-trioxolan via the zwitter-ion must be recognised as the only correct one. The Criegee mechanism has been confirmed experimentally by the incorporation of the ^{18}O isotope label exclusively in the ether bridge of the ozonide in the joint ozonolysis of an olefin and the labelled aldehyde.

At the same time the initial Criegee mechanism[4] could not explain the dependence of the ratio of the ozonolysis products (ozonides, aldehydes, and peroxides) on the stereochemistry of the initial olefins[60]. According to Criegee's theory, the geometry of the initial olefin should not have influenced the composition of the ozonolysis product, because the same intermediate is formed from both isomers. Subsequent studies showed that ozonides can exist in the *cis*- and *trans*-forms and that the ratio of both "intrinsic" and "cross" isomers depends on the configuration of the initial olefin[61,62].

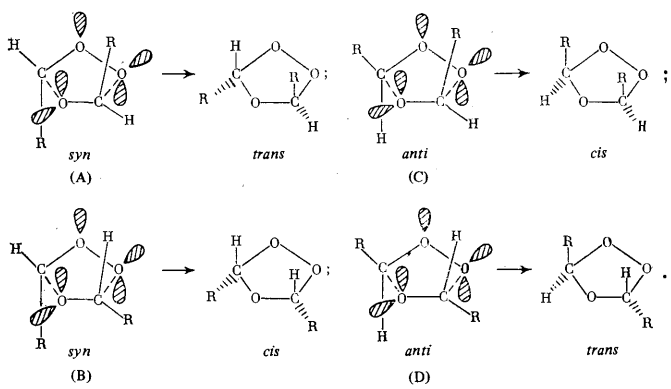
The configuration of a symmetrical disubstituted ozonide is determined by resolving it into its enantiomers. By obtaining one of the optically active forms of one of the isomers

of 3,5-di-isopropyl-1,2,4-trioxolan, it was possible to conclude, for example, that the given isomer has the *trans*-configuration[63], because the *cis*-isomer is a *meso*-form and cannot be resolved into enantiomers. The configurations of a series of isomeric oxonides have been established by their chromatographic separation on acetylcellulose[64,65]. The ratio of the *cis*- and *trans*-ozonides can be determined from ^{1}H NMR spectra, provided that the spectrum of each configuration is known.

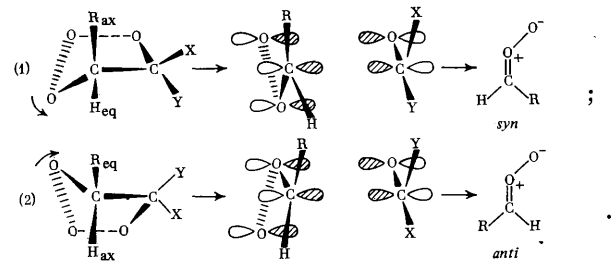
In order to explain the stereospecificity of the formation of ozonides, the existence of the zwitter-ion in the *syn*- and *anti*-configurations has been postulated[66], which was also assumed much earlier by Criegee[67]. Developing this theory, Lattimer et al.[15] considered the cyclodecomposition reactions of the primary ozonide and the cycloaddition of the zwitter-ion to the carbonyl group from the standpoint of the Woodward–Hoffmann theory, according to which ozone and the zwitter-ion are isoelectronic and have a π-system comprising four electrons. Correspondingly the π-systems of the alkene and the carbonyl compound have two electrons. Consequently the reactions involving the formation of the primary and final ozonides can be classified as supra,supra-addition of the 4π- and 2π-systems, which obeys the symmetry laws:



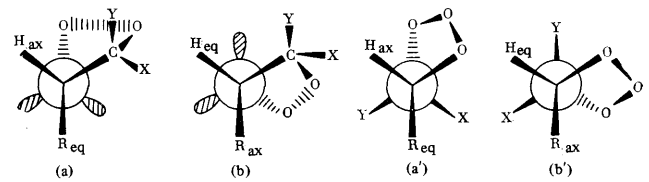
At the instant when the carbonyl group approaches the *syn*-zwitter-ion, the substituents R in the transition state can be oriented in two ways—(A) and (B). The transition state (A) is converted into the *trans*-ozonide and the transition state (B) is converted into the *cis*-ozonide. For the *anti*-zwitter-ion, the transition state model (C) gives rise to the *cis*-configuration of the ozonide and model (D) gives rise to the *trans*-configuration. Evidently models (A) and (C) should be preferable, because the bulky groups of the aldehyde in this case interact less strongly with the free electron pair at the terminal oxygen atom of the zwitter-ion. As a consequence of this, the *syn*-zwitter-ion is converted preferentially into the *trans*-ozonide, while the *anti*-zwitter-ion is converted into the *cis*-ozonide:



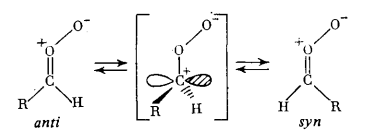
For the decomposition of the primary ozonide into the zwitter-ion and the carbonyl group, it is necessary that the oxygen adjoining the carbon atom converted into the zwitter-ion should be displaced from the "plane" of the ring of the primary ozonide. This transition state has the envelope conformation with axial (pathway 1, leading to the *syn*-zwitter-ion) or equatorial orientation of the substituent R (pathway 2, leading to the *anti*-zwitter-ion):



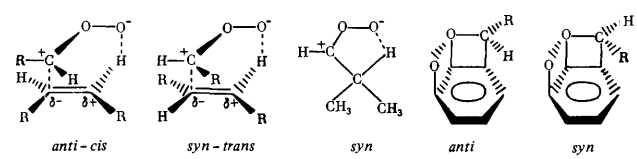
In order to determine which pathway is preferred for a specific olefin, it is sufficient to know the relative stabilities of the two possible transition states. In an estimate of this kind one must take into account the interactions of the substituent with the ring and with another substituent at the neighbouring carbon atom. These interactions are clearly seen in Newman's projection formulae with C–O (formulae a and b) and C–C (formulae a′ and b′) axes:



The zwitter-ion formed can isomerise to a zwitter-ion with the opposite configuration despite its short lifetime[68]:



It is known that specific solvation plays a significant role in the oxidation reactions of organic compounds[69]. It has been noted that the solvent and the olefin can stabilise the zwitter-ion by forming hydrogen bonds[70]. This effect is suppressed by an aromatic hydrocarbon[68], which can form a complex with the zwitter-ion, preventing or retarding its isomerisation:



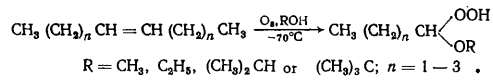
The detection of complex formation and the reversible interconversion of stereoisomeric carbonyl oxides is important for the understanding of the fine structure of the zwitter-ion. Recent calculations[31] showed that both ozone and the carbonyl oxide are singlet biradicals in their ground states. However, there is no experimental evidence for the formation of products of the reactions of the singlet biradical carbonyl oxide. For example, in the decomposition of *trans*-di-t-butyl-1,2,3-trioxolan in cumene or oct-4-ene, which are sensitive to radicals, no radical reaction products were detected[71]. Nor was it possible to detect radicals when the thermal decomposition of the same primary ozonide was followed with the aid of EPR.

Thus the hypothesis of the existence of the zwitter-ion in the *syn*- and *anti*-configurations explains satisfactorily the experimental facts obtained hitherto, including the stereochemical features of the formation of ozonides. The attempt to show that the main intermediate in the ozonisation of olefi is a singlet biradical have not been supported by rigorous experimental data.

III. THE INFLUENCE OF THE STRUCTURE OF OLEFINS AND OZONIZATION CONDITIONS ON THE STRUCTURE OF PEROXY-PRODUCTS OF OZONOLYSIS

The solvent has a decisive influence on the structure of the peroxy-product of ozonolysis. In the ozonisation of olefins in proton-donating solvents (alcohols, carboxylic acids, and water) the zwitter-ion is as a rule stabilised by the addition of a solvent molecule, giving rise to α-substituted hydroperoxides[11,16,72].

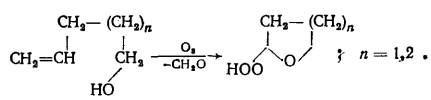
Individual alkoxyhydroperoxides have been isolated from the peroxy-products of the ozonolysis of symmetrical olefins[73]:



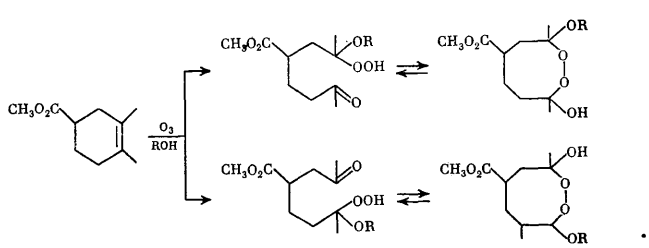
$R = CH_3$, C_2H_5, $(CH_3)_2CH$ or $(CH_3)_3C$; $n = 1-3$.

In the ozonisation of *cis*-octadec-9-ene in various alcohols (C_1–C_{16}) and monocarboxylic acids (C_2–C_{18}) or in an inert solvent containing the same alcohols or carboxylic acids in equimolar proportions, the products are the corresponding α-alkoxy- and α-acyloxy-hydroperoxides[74]. Symmetrical di-(α-hydroxyalkyl) peroxides have been obtained by the ozonisation of α-olefins in aqueous acetone[75].

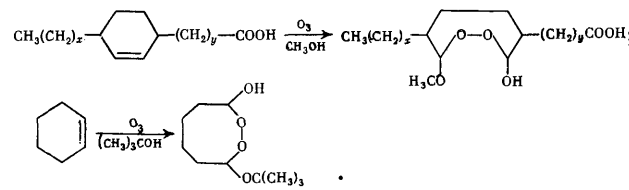
If the proton-donating group is present in the olefin molecule itself, it is involved in the stabilisation of the zwitter-ion[76]. When its position is favourable for the formation of five- or six-membered rings, such stabilisation becomes preferential[77]:



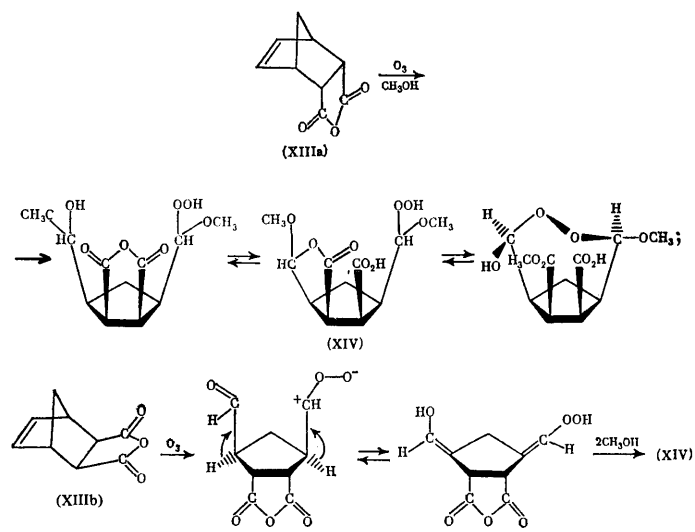
The interaction of the hydroperoxy- and formyl groups leads to the formation of α,α′-disubstituted peroxides. Depending on the nature of the olefin, the products of this reaction can have different structures. Whereas monomeric compounds are formed preferentially from linear olefins[78], in the case of cyclohexene derivatives the main products are oligomeric hemiperacetals[79,80]. However, monomeric cyclic peroxides are formed from cyclohexenes with bulky substituents[81,82]:



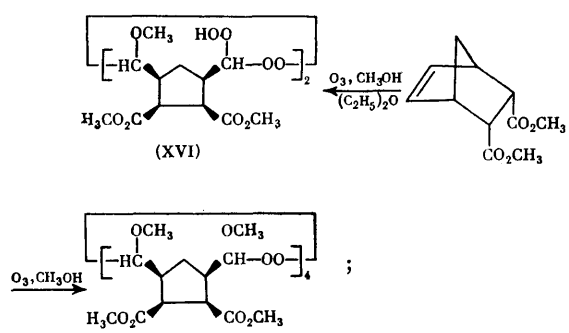
Monomeric α-methoxyhydroperoxides are obtained in the ozonisation of alkylidene- and benzylidene-adamantanes in methanol[83]. The mode of the intramolecular interaction of the hydroperoxy- and formyl groups can be regulated by the presence of bulky substituents next to the double bond[84] or by alcoholic groups[81]:

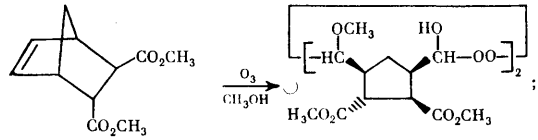


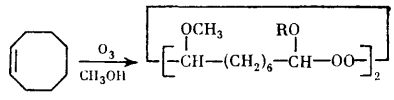
If the formyl and hydroperoxy groups are close together, as, for example, in the ozonolysis product of norbornene[85], then the monomeric hemiperacetal is the main reaction product, while in the ozonisation of carboxy-derivatives of norbornene one obtains exclusively monomeric peroxy-compounds as a consequence of the involvement of the carboxy-groups in the intramolecular interaction[86]. The formation of the same peroxy-product from the *endo*-, *cis*-, and *exo*, *cis*-anhydrides (XIIIa) and (XIIIb) is evidence for the isomerisation of the formyl groups:



On the other hand, in the ozonisation of the dimethyl esters of the stereoisomeric bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic acids the products are exclusively oligomeric peroxides, the degree of oligomerisation being influenced by the stereochemistry of the methoxycarbonyl groups[87]. The reaction involving cyclo-octene yielded a cyclic bishemiperacetal (XV).[88] If the ozonisation of olefins is carried out in an ethereal solvent, the peroxide ozonolysis products (XVI) and (XVII), with an enhanced content of active oxygen, are formed[87,88]:

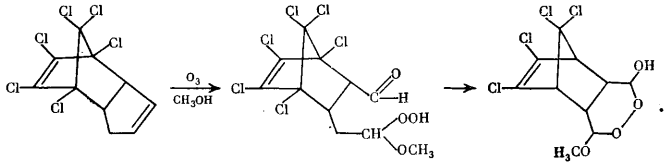




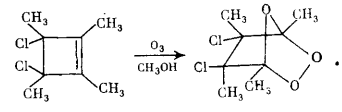


R = H (XV) or OH (XVII).

As a consequence of the deactivation of one of the double bonds by chlorine atoms, hexachlorobicyclopentadiene[89] and hexachlorobicycloheptadiene are attacked by ozone only at the unsubstituted double bond[90]:

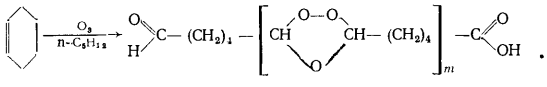


The steric influence can be so great that in the ozonisation of, for example, a substituted cyclobutene in methanol the attack on the zwitter-ion by the solvent is ruled out and the corresponding ozonide is formed[91]:



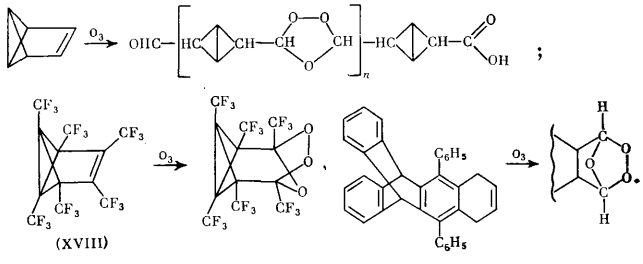
When tetraphenylethylene is ozonised in a mixture of chloroform and methanol, the product is the bishydroperoxide of diphenylmethane instead of the expected methoxyhydroperoxide[92].

The main products of the ozonisation of acyclic olefins in inert solvents are monomeric ozonides[34,93], but oligomeric ozonides are also formed. The yield of the latter depends on the solvent polarity and the structure of the olefin[34,94]. Oligomeric products are obtained almost exclusively from sterically unhindered six-membered olefins[95]:



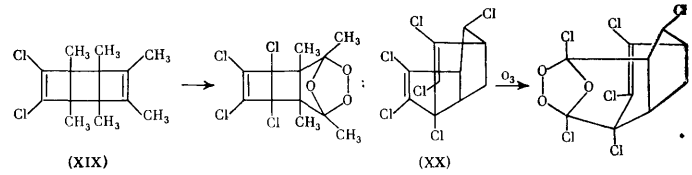
The ozonisation of cyclopentene and cyclobutene gives rise to monomeric ozonides[18,96-98], although the formation of oligomers in this case too has been noted[95].

Oligomeric ozonides are obtained from hexachlorobicyclo-[2,2,1]hepta-2,5-diene[90] and benzvalene[99]. However, the hexakis(trifluoromethyl) derivative (XVIII) gives a high yield of the monomeric ozonide[100]. For steric reasons, monomeric ozonides are also formed from polynuclear hydroaromatic hydrocarbons[101]:



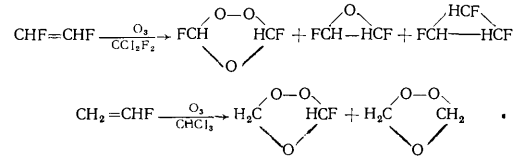
(XVIII)

In the presence of double bonds with electron-donating and electron-accepting substituents [for example, in compound (XIX)] the bond with the higher electron density is attacked[89]. In the polycyclic compound (XX) one of the chloro-substituted double bonds was ozonised[102]:

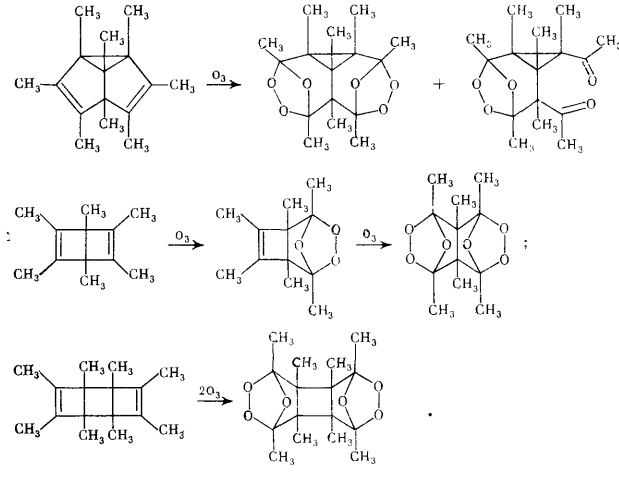


(XIX) (XX)

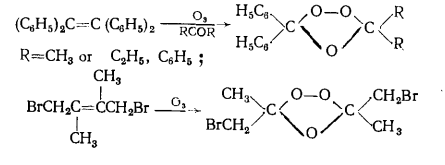
The ozonisation of *cis*- and *trans*-1,2-difluoroethylenes gives rise to a mixture of the ozonide (30%), the epoxide (15%), and trifluorocyclopropane (0.4%),[103] while fluoroethylene yields a mixture of ozonides[104]:



The corresponding diozonides are formed in the ozonisation of octamethylsemibullvalene[96,105], hexamethylbicyclo[2,2,0]-hexa-2,5-diene[106], and octamethyltricyclo-octadiene[107]:

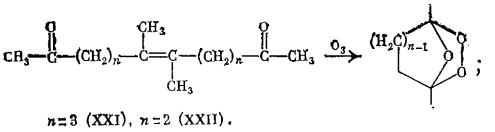


Trisubstituted[108] and tetrasubstituted[109] "cross" ozonides have been synthesised by the ozonisation of appropriately substituted olefins in the presence of an excess of the ketone. If the keto-group, arising on cleavage of the olefin, is activated by an electronegative substituent, then "intrinsic" ozonides are formed in a high yield[110]:



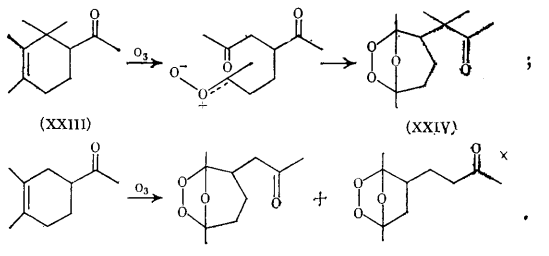
When a keto-group is present in the olefin molecule, there is competition between intramolecular and intermolecular reactions. Thus, in the ozonisation of the diketoalkenes (XXI) and (XXII), the intramolecular reaction of the zwitter-ion

predominates and the ozonides of dimethylcyclopentene and dimethylcyclobutene respectively are formed in high yields[111]:



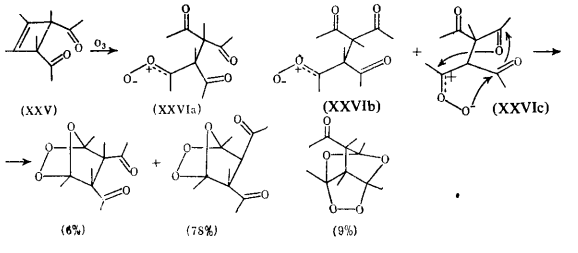
$n=3$ (XXI), $n=2$ (XXII).

In the ozonisation of ketocyclo-olefins intramolecular competition of the two carbonyl groups is observed. Owing to the steric hindrance by the geminal methyl groups in "Dallacker's" ketone (XXIII) only the ozonide of the substituted cyclopentene (XXIV) is formed; in the absence of these methyl groups, the corresponding ozonides of both cyclopentene and cyclobutene are obtained[112]:



(XXIII) (XXIV)

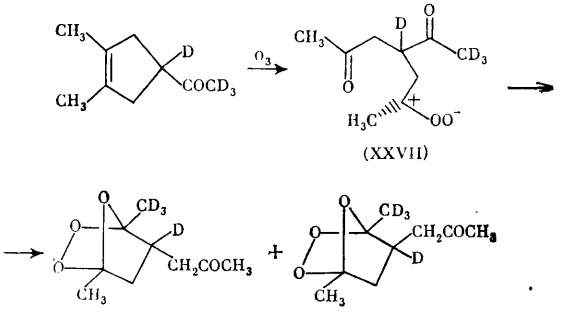
The zwitter-ion formed in the ozonisation of the symmetrically substituted cyclobutene (XXV) can have different conformations (XXVI, a–c), which lead to three products respectively[113]:



(XXV) (XXVIa) (XXVIb) (XXVIc)

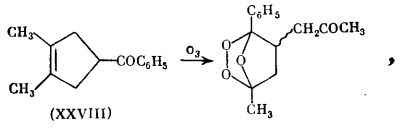
(6%) (78%) (9%)

In the zwitter-ion (XXVII), which contains two acetyl groups, there is interaction with the nearest acetyl group, because this leads to the more stable ozonide of cyclobutene[26]:

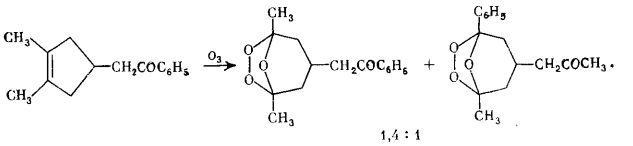


(XXVII)

For the same reason, in the ozonisation of compound (XXVIII) the reaction of the zwitter-ion with the benzoyl group and not with the more reactive acetyl group takes place preferentially. If the carbonyl groups are located in equivalent positions, the acetyl group is the more reactive[26]:

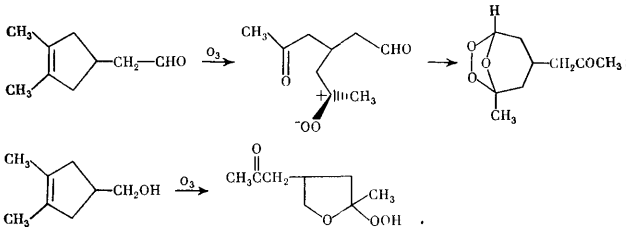


(XXVIII)

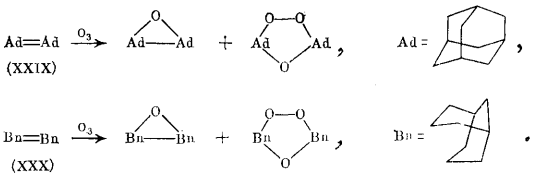


1,4 : 1

If a formyl or hydroxy-group is present, the zwitter-ion reacts with them and not with the acetyl group[26]:

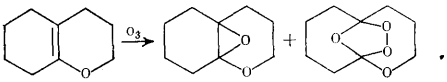


Sterically hindered olefins give rise to epoxides as well as ozonides. In the ozonisation of the alkenes (XXIX) and (XXX) the corresponding epoxides are formed preferentially instead of the expected methoxyhydroperoxides even in the presence of methanol[114]:

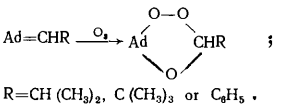


(XXIX) (XXX)

An analogous behaviour has been observed in the ozonisation of tetrahydrochromone[115]:

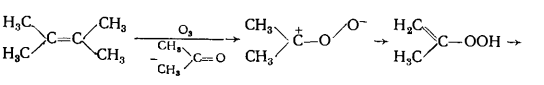


The steric hindrance may be so great that the double bond becomes inert towards ozone. Thus, whereas isopropyl-, t-butyl-, and phenyl-methyleneadamantanes normally give rise to ozonides, the replacement of the vinyl hydrogen atom by the t-butyl or phenyl group makes these compounds resistant to ozone[114]:

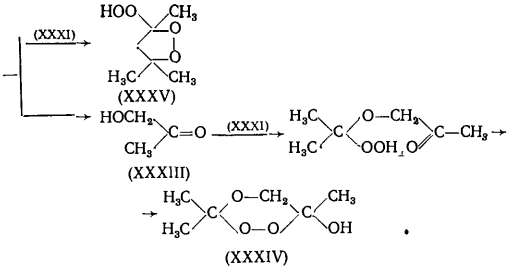


R=CH $(CH_3)_2$, C $(CH_3)_3$ or C_6H_5.

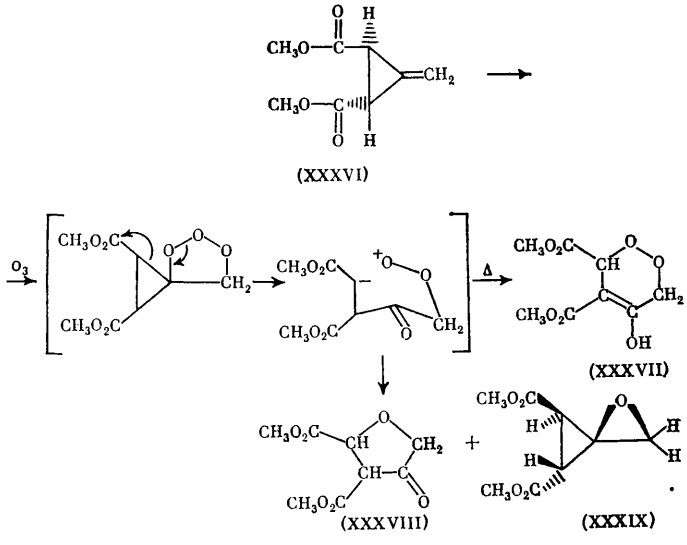
Certain zwitter-ions can be stabilised by isomerisation or rearrangement, which leads to anomalous peroxide or non-peroxide ozonolysis products. Thus the zwitter-ion (XXXI), formed in the ozonisation of tetramethylethylene, isomerises to the α-hydroxyketone (XXXIII) via the vinyl hydroperoxide (XXXII). This results in the formation of the six-membered trioxan (XXXIV) [109] or the cyclic hydroperoxide (XXXV):[116]



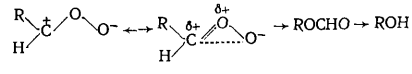
(XXXI) (XXXII)



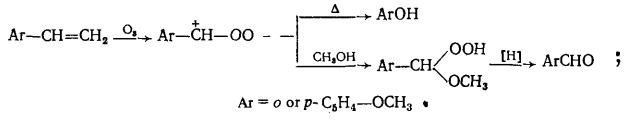
The ester of Feist's acid (XXXVI) is ozonised anomalously, being converted into a mixture of compounds (XXXVII)–(XXXIX). Evidently the peroxide (XXXVII) is the isomerisation product of the zwitter-ion[117]:



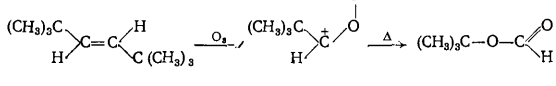
Anomalous ozonolysis products are usually observed when the zwitter-ion contains a group with a tendency towards migration[16]:



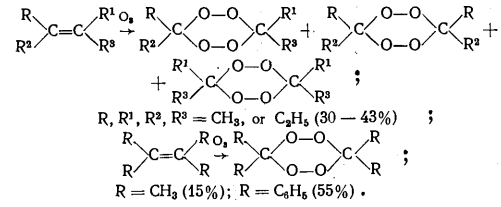
Such rearrangements are characteristic of zwitter-ions generated from substituted styrenes[118]. On the other hand, if the zwitter-ion is bound by methanol, anomalous products are not formed[119]:



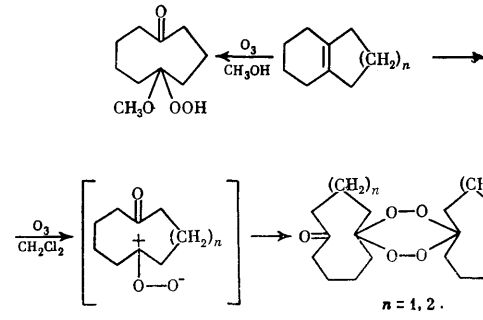
Alkyl groups show a much smaller tendency towards migration. In the ozonisation of even *trans*-di-t-butylethylene only 5% of t-butyl formate is formed[118]:



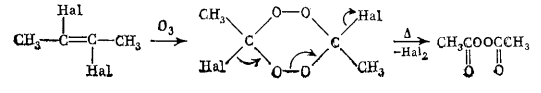
When the reaction is carried out in inert solvents, the formation of dimeric and oligomeric peroxides together with ozonides is frequently noted[32,110,120]. The yield of these compounds depends greatly on the structure of the olefin. Thus, whereas in the ozonisation of α-olefins only traces of dimeric peroxides are formed[11,16], dimeric normal and cross peroxides are obtained from tetrasubstituted ethylenes in yields ranging from 15 to 55%.[121]



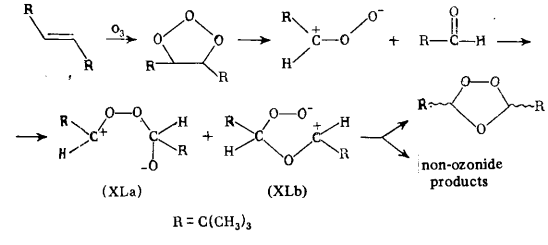
The dimerisation of the zwitter-ion derived from 4,5,6,7-tetrahydroindan[122] and 9,10-octalin[123] leads to the corresponding cyclic diperoxides. The dimerisation does not occur when the ozonisation is carried out in methanol[122]:



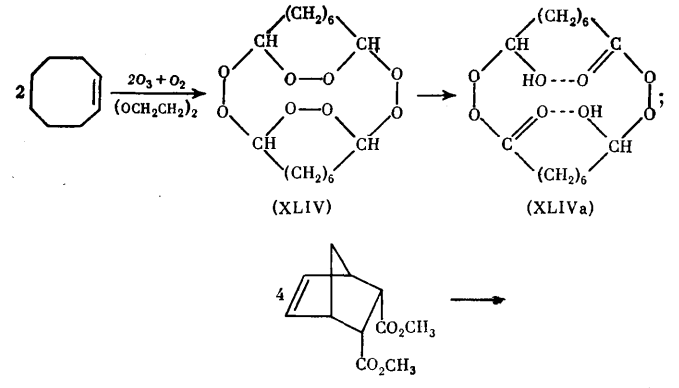
Diacetyl peroxide is obtained from *trans*-2,3-dibromobut-2-ene, probably via an intermediate cyclic diperoxide[124]. The crystalline dimeric α-chloroperoxide has been isolated in the reaction of the dichloro-derivative[125]:



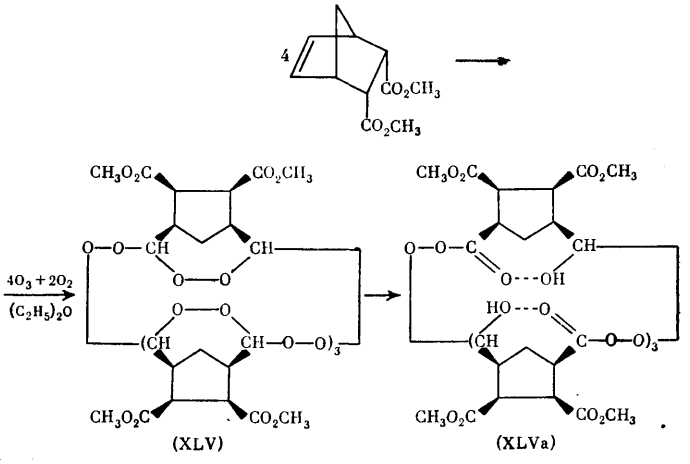
The influence of the solvent on the formation of ozonides has been studied in detail in relation to *trans*-di-t-butylethylene[71]. It has been shown that the ozonide is formed only in non-polar solvents (hydrocarbons), while in methylene chloride, trichlorofluoromethane, acetone, and ethyl acetate it is not formed at all. Ozonisation in diethyl ether at −75 °C does not give rise to the ozonide, but at a lower temperature (−90 °C) it is possible to obtain the ozonide in 25% yield. The addition of an extraneous aldehyde reduces the yield of both the normal and "cross" ozonides. These results have been explained by the stepwise recombination of the zwitter-ion and the aldehyde. In a non-polar solvent the intermediate (XLa) [71] or (XLb) [126] cyclises to the ozonide, while a polar solvent solvates it, increasing the lifetime and probability of side reactions (reactions with the carbonyl oxide and aldehyde as well as polymerisation)[71]:



An oligomeric intermediate of type (XLa) or (XLb) solvated by a polar ethereal solvent can undergo further oxidation, which in the ozonisation of cyclic olefins leads to the peroxide ozonolysis products (XLIV) and (XLV),[88,127] which isomerise to the α-hydroxyperesters (XLIVa) and (XLVa):



(XLIV) (XLIVa)



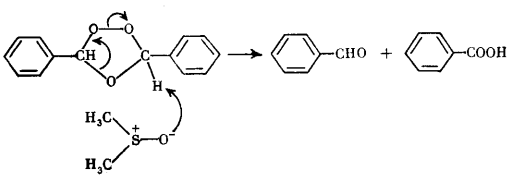
(XLV) (XLVa)

IV. REACTIONS OF PEROXY-PRODUCTS OF OZONOLYSIS

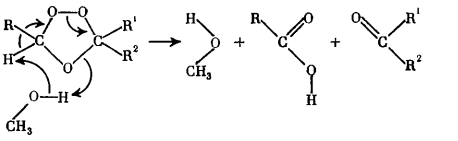
In the ozonisation of olefins a degree of oxidation intermediate between an aldehyde and carboxylic acid is attained. The reactions of ozonides and other peroxy-products of ozonolysis can be divided into two types: those occurring without a change in the degree of oxidation attained (cleavage reactions) and those with a change in the degree of oxidation (oxidation and reduction reactions).

The mode of decomposition of peroxy-compounds depends significantly on the nature of the solvent[69]. The acidity of the medium also influences hydrolysis, solvolysis, alcoholysis, and acidolysis.

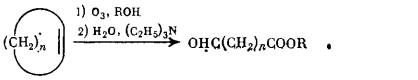
The usual products of the cleavage of ozonides are the corresponding aldehydes and carboxylic acids[16,34]. In an aqueous medium ozonides are cleaved with difficulty[16], but under the influence of strongly solvating solvents (dimethyl sulphoxide, dimethylformamide, and amines) the fragmentation of stilbene ozonide proceeds rapidly and quantitatively[128]:



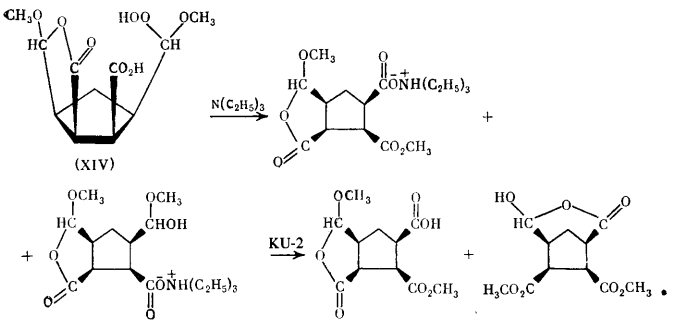
In methanol and benzyl alcohol the rate of fragmentation of ozonides is significantly higher than in benzene, di-isopropyl ether, dioxan, and tetrahydrofuran[65,129]. The solvolysis of ozonides proceeds at identical rates in neutral and weakly acid media, while in an alkaline solution the process is accelerated. The isotope effect observed in the methanolysis of deuterated ozonides[65] shows that the stage involving the elimination of a proton from the trioxolan ring is rate-determining. The exceptional role of the alcohol in the fragmentation of ozonides can be explained by the fact that it behaves simultaneously as a "base" and an "acid"[65]:



α-Substituted hydroperoxides are cleaved more readily than ozonides[130]. Thus the hydrolysis of alkoxyhydroxyperoxides derived from cyclic olefins gives rise to the esters of the corresponding ω-formylcarboxylic acids in 85% yield[131]:

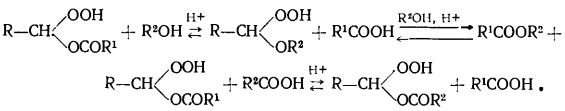


The isomerisation of the hydroperoxy-group to the carboxylate group has been observed in the interaction of the peroxide (XIV) with triethylamine[86]:

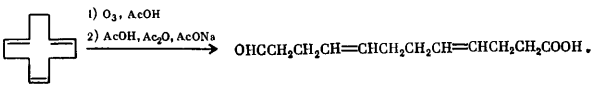


(XIV)

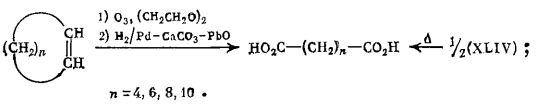
α-Acyloxyhydroperoxides undergo transesterification[132]:



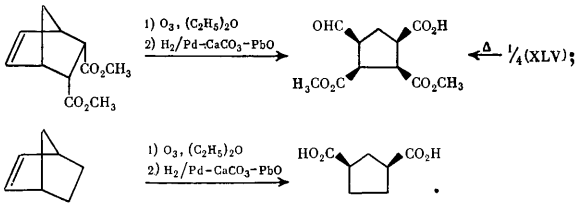
The acidolysis of the product of the controlled ozonolysis of cyclic polyolefins in acetic acid leads to unsaturated ω-formylcarboxylic acids[133]:



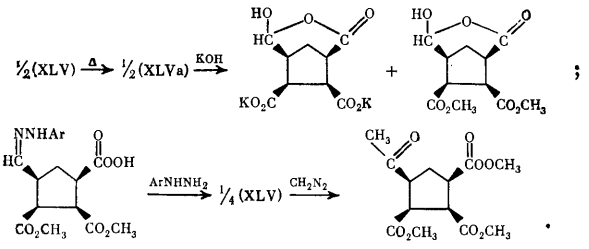
The isomerisation and cleavage of peroxides with a high content of active oxygen, which are formed in the ozonisation of cyclo-olefins in ethereal solvents[88], leads to the corresponding α,ω-dicarboxylic acids, which constitutes a new method of synthesising carboxylic acids without the need for an additional oxidation stage after ozonisation[134-136]:



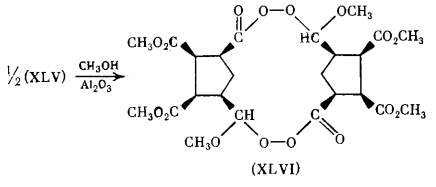
The fragmentation of the peroxide (XLV) yields the corresponding formylcarboxylic acid, while the ozonolysis of 2-norbornene in an ethereal solvent results in the formation of *cis*-cyclopentane-1,3-dicarboxylic acid[127]:



The fragmentation of the peroxide (XLV) also takes place in an alkaline solution and its interaction with diazomethane or 2,4-dinitrophenylhydrazine leads to the formation of peracid groups[127]:

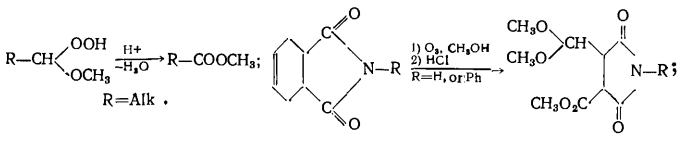


On being eluted with methanol from alumina, the tetrameric peroxide (XLV) is converted[127] into the dimeric α-methoxyperester (XLVI):

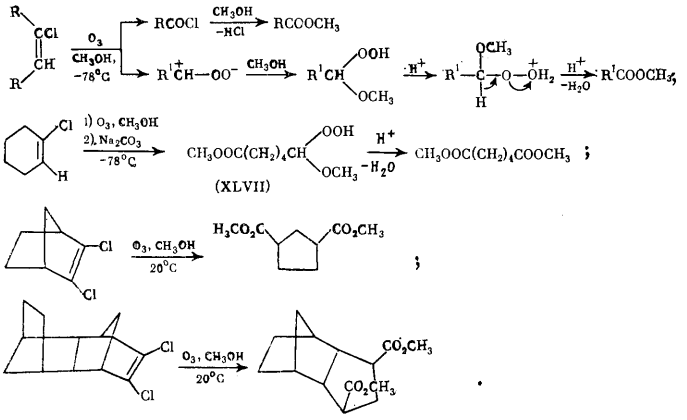


(XLVI)

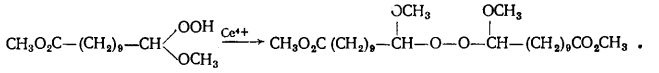
Alkoxyhydroperoxides derived from trisubstituted and asymmetrically disubstituted olefins hydrolyse rapidly to the corresponding ketones and alcohols[137]. Peroxides obtained from symmetrically disubstituted olefins do not give high yields of aldehydes under these conditions. Treatment with hydrogen chloride converts methoxyhydroperoxides quantitatively into the methyl esters of the corresponding carboxylic acids[138]. Derivatives of ω-formylcarboxylic acids have been obtained under these conditions from certain cyclic olefins[139]:



The peroxides formed in the ozonisation of chloro-olefins in methanol readily decompose into the corresponding methyl carboxylates. By neutralising the hydrogen chloride evolved, it is possible to isolate the methoxyhydroperoxide (XLVII):[138,140]

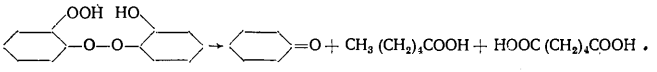


Oxidation of α-alkoxyhydroperoxides with cerium ammonium nitrate leads to the crystalline dialkoxyperoxides[129]:

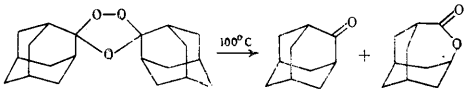


As in hydrolysis, the main products of the thermal decomposition of ozonides are the corresponding aldehydes and carboxylic acids[1,11,141].

When α-hydroperoxy-α-hydroxydicyclohexyl peroxide is heated in boiling toluene, cyclohexanone is formed preferentially (25%) and there are lower yields of caproic (8%) and adipic (4%) acids[28]:

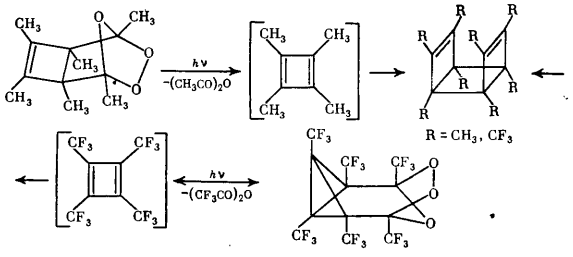


Thermal, and recently also photochemical, cleavage of ozonides has become a promising trend in organic synthesis[142]. Thus the thermolysis[96,142] of bisadamantylidene ozonide leads to the formation of adamantanone and the lactone (XLVIII):[114]

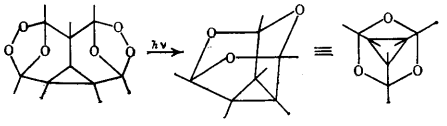


(XLVIII)

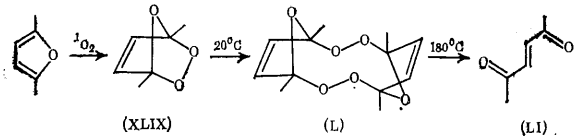
The photolysis of the mono-ozonides of Dewar hexamethylbenzene[143] and hexakis(trifluoromethyl)benzvalene[100] leads to the *syn*-dimers of tetramethyl- and tetrakis(trifluoromethyl)-cyclobutadiene:



The photolysis of the diozonide of octamethylsemibullvalene results in the formation of a triketal of a new type[103]:

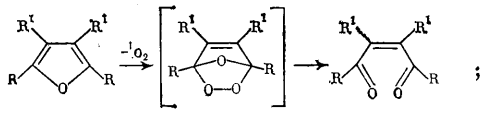


Ozonides can be synthesised by methods other than the ozonisation of olefins[120]. The method involving the oxidation of furan derivatives with singlet oxygen[144], which can be readily obtained, for example, from the adduct of ozone with triphenyl phosphite[145,146] or with certain other compounds[147], is of special interest. The [4 + 2] cycloaddition results in the formation of the mono-ozonides of substituted cyclobutadienes[142]. Thus the photoxidation of 2,5-dimethylfuran yields the ozonide (XLIX), which is converted at room temperature into the stable dimer (L), the latter decomposing into the dione (LI) only at a high temperature[144]:



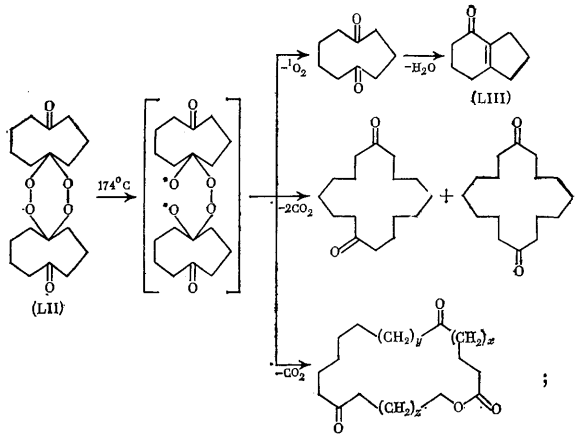
(XLIX) (L) (LI)

The photoxidation of substituted furans can be regarded as a general method of synthesis of *cis*-diacylolefins[142]:



R = R¹ = H; R = R¹ = C_6H_5; R = CH_3, R¹ = H; R = C_6H_5, R¹ = H .

The thermolysis and photolysis of cyclic di- and tri-peroxides have been considered in reviews[142,148]. Such peroxides are usually synthesised by the reaction of cycloalkanones with hydrogen peroxide[149]. In the ozonolysis of certain olefins they are formed as a consequence of the dimerisation of the zwitter-ion. The thermal or photochemical fragmentation of cyclic diperoxides leads to carbocyclenes, lactones, and cyclic ketones[142]. Thus the diperoxide (LII), obtained by the ozonolysis of 4,5,6,7-tetrahydroindan, is converted on heating in boiling decane into cyclononane-1,5-dione (18%), [cyclising to compound (LIII) during isolation], a mixture of cyclohexadecane-1,8-dione and cyclohexadecane-1,9-dione (50%), and four isomeric dioxoheptadecanolides (16%):[122]



(LII) (LIII)

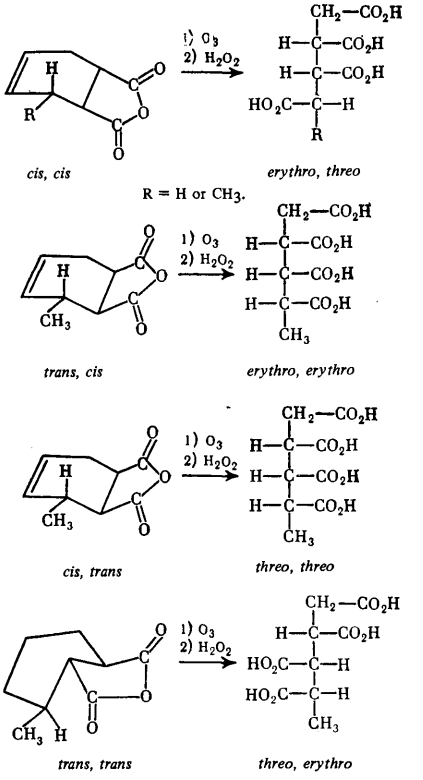
x = 1, y = 3, z = 1; x = 1, y = 2, z = 2; x = 2, y = 2, z = 1; x = 2, y = 1, z = 2 .

The reactions of ozonolysis peroxy-products under the influence of oxidants or reductants are widely used in preparative organic synthesis[16,34,150] and have already found application in industrial technology[1,151]. The oxidative decomposition of peroxy-products of ozonolysis takes place in two stages: the oxidation proper and thermal decomposition of peroxides. In the synthesis of carboxylic acids the two stages are combined or are arbitrarily divided in terms of temperature conditions#.

Oxidative decomposition occurs under the influence of oxygen at an elevated temperature. In this case oxidation initiators or catalysts (ozone, variable-valence metal compounds[1,16,153–159], inorganic salts in polar aprotic solvents[160], and aminoacids[161]) are used. The oxidants consist of a suspension of silver oxide in an alkaline solution[1,34,35], potassium permanganate[162], chromic acid[163], and nitric acid[164]. However, hydrogen peroxide usually employed as a mixture with formic or acetic acid, is the most convenient and most widely used reagent[1,35,150,165–167]. Investigators have paid particular attention to the synthesis of aliphatic α,ω-dicarboxylic acids[168,169], which are of greatest practical interest[1,170,171]. Methods combining the ozonisation and oxidation stages have been developed[1,35,172].

The ozonolytic synthesis of polycarboxylic acids and other polyfunctional compounds has been studied to a lesser degree. When the molecule contains several functional groups, they interact and complicate the oxidative decomposition. In the ozonolysis of cyclic polyenes or cyclo-olefins containing functional groups, catalysts increasing the process selectivity are therefore used.

The isomeric butane-1,2,3,4-tetracarboxylic[174–176] and pentane-1,2,3,4-tetracarboxylic[177,178] acids have been synthesised by the ozonolysis of the stereoisomeric Δ^4-tetrahydro- and 3-methyl-Δ^4-tetrahydro-phthalic acids[173]:



cis, cis — *erythro, threo*

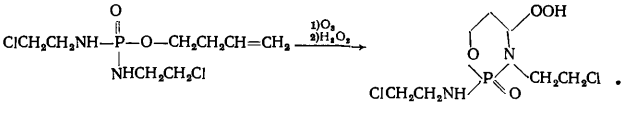
R = H or CH_3.

trans, cis — *erythro, erythro*

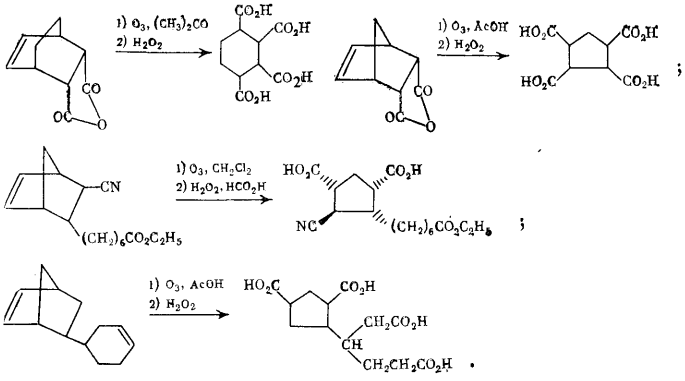
cis, trans — *threo, threo*

trans, trans — *threo, erythro*

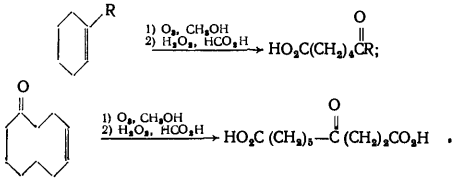
#In the ozonolysis of the alkenyl esters of phosphorodiamidic acids, peroxy-compounds were isolated after the first oxidative decomposition stage[152]:



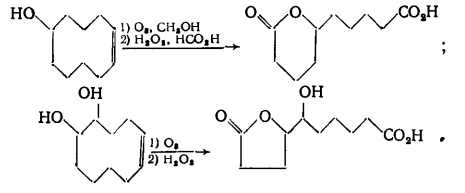
Cyclic polycarboxylic acids have been obtained from derivatives of bicyclic olefins[179–181] and tricarboxylic acids have been synthesised from alkenylcyclohexenes[182]:



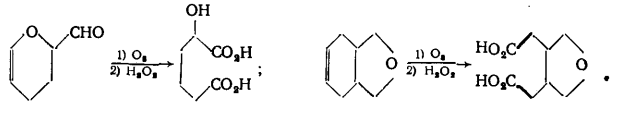
Ketocarboxylic and ketodicarboxylic acids have been obtained by the oxidative ozonolysis of 1-alkylcycloalkenes[183] and cycloalkenones[184] respectively:



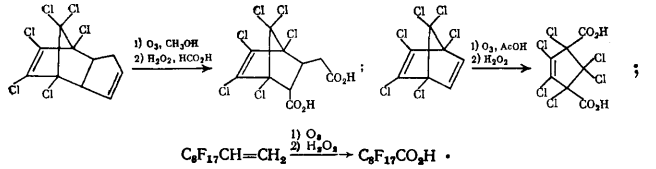
The ozonolysis of cyclo-olefins containing a hydroxy-group led to lactones whose hydrolysis constitutes a pathway to hydroxydicarboxylic acids[185,186]:



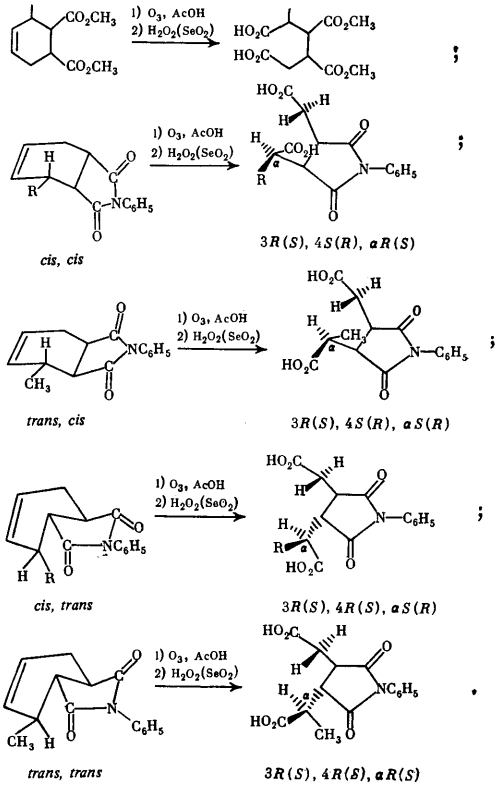
An α-hydroxydicarboxylic acid has been obtained from the acrolein dimer[187], while tetrahydrofuran derivatives have been synthesised from a cycloalkene condensed with a heterocycle[188]:



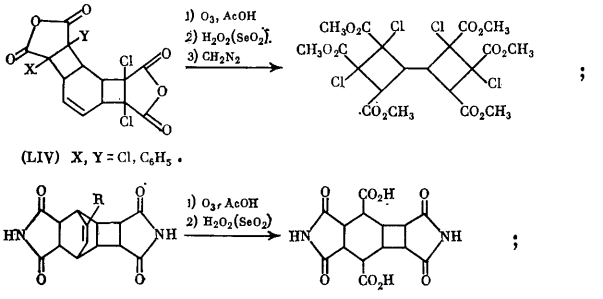
In order to synthesise polychloro-[89,90,189] and polyfluoro-derivatives[190] of di- and mono-carboxylic acids, the corresponding halogeno-derivatives of olefins have been ozonised:



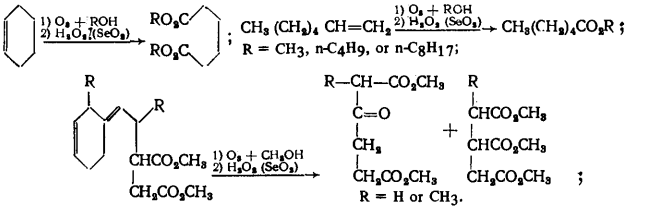
The oxidative decomposition of peroxy-products of ozonolysis, carried out by treatment with hydrogen peroxide, can be accelerated with the aid of selenium dioxide[191–193], in the presence of which the process proceeds under milder conditions with a higher selectivity. This makes it possible to increase the yield by 10–30% as well as the purity of the aliphatic polycarboxylic acids. Thus the 2,3-dimethyl ester of pentane-1,2,3,4-tetracarboxylic acid[191–193] and the corresponding stereoisomeric 3,4-disubstituted *N*-phenylpyrrolidine-2,5-diones[194–196] have been synthesised from the dimethyl ester and the stereoisomeric *N*-phenylimides of Δ^4-tetrahydrophthalic acid and its 3-methyl derivative:



The use of selenium dioxide permitted the successful ozonolysis of the polycyclic compounds (LIV) and (LV):[197,198]

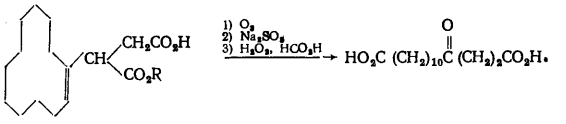


The oxidative decomposition of the peroxy-products of the ozonolysis of olefins in the corresponding alcohols led to the formation of carboxylic acid esters[193,199,200]:

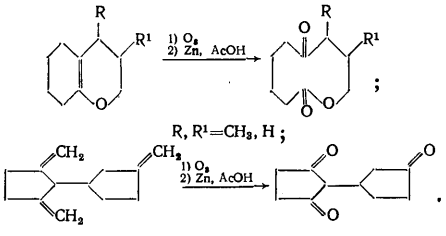


The copolymers of butadiene with isobutene[150,201,202] and styrene[203] have been converted by oxidative ozonolysis with participation of pyridine into the corresponding oligomers with terminal carboxy-groups. 3-Phenyladipic acid has been synthesised by the selenium dioxide-catalysed oxidative decomposition of the peroxy-product of the ozonolysis of regular butadiene–styrene rubber[204,205].

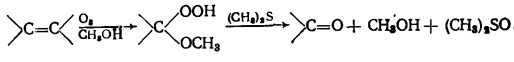
The peroxy-products of ozonolysis are sometimes subjected to preliminary reduction in order to facilitate the oxidative decomposition[206]:



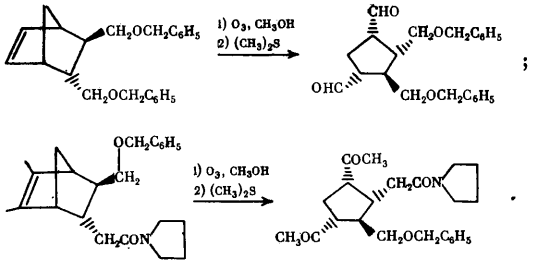
Various reductants, used to convert the peroxy-products of ozonolysis into aldehydes and ketones, have been listed in a number of reviews[16,34,207]. Among traditional reagents, sodium bisulphite[208], the lower-valence metal salts[209–211], alkali metal iodides[212], and sodium thiosulphate[213,214] have been used in recent years. Among inorganic reductants, zinc dust has been most often employed[215–219], for example, in the reductive ozonolysis of tetrahydrochromone derivatives[220] and the cyclo-oligomers of allene[221]:



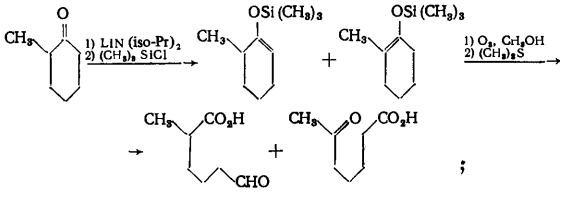
Organic reductants have been used on an increasingly wide scale in recent years. Dimethyl sulphide[222–224] and sometimes other dialkyl sulphides or thiacyclanes[225,226] have been used to synthesise alkoxyhydroperoxides:

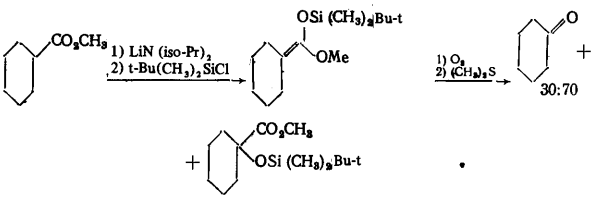


Dimethyl sulphide has been introduced into practical fine organic synthesis[227–230], for example, the synthesis of the intermediates for prostaglandins[231,232]:

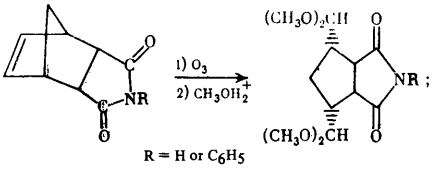


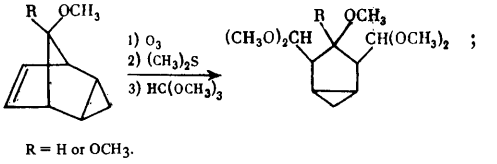
Ozonolysis has found an interesting application for the cleavage of ketones and carboxylic acids via the trimethylsilyl ethers of their enolic forms[233]:



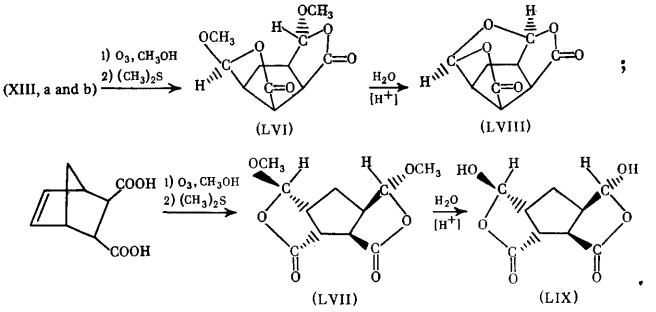


Aldehydes can sometimes be more conveniently isolated in the form of acetals[139,234–236]:

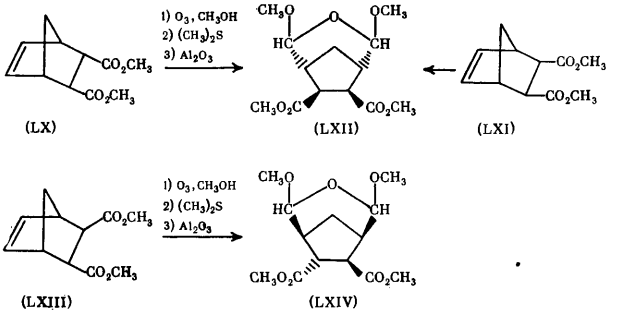




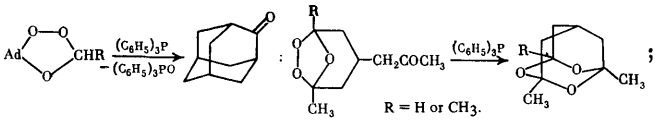
Under the influence of dimethyl sulphide, the peroxy-products of the ozonolysis of the *endo*-, *cis*- and *exo,cis*-anhydrides (XIII, a and b) give rise to the same *syn*-3,5-bis-(methoxymethyl)dilactone (LVI), while the *endo,exo*-diacid gives rise to the *anti*-isomer (LVII) under analogous conditions[237]. In the presence of water both the ozonolysis peroxy-products and the dilactones (LVI) and (LVII) are converted into oxygen-containing polyheterocyclic compounds (LVIII) and (LIX) respectively[86,237]:



The peroxy-products of the ozonolysis of the *endo,cis*- and *exo,cis*-diesters (LX) and (LXI) are converted on treatment with dimethyl sulphide into the same product (LXII), while the isomeric compound (LXIV) is formed under analogous conditions from the *endo,exo*-isomer (LXIII):[87,127]

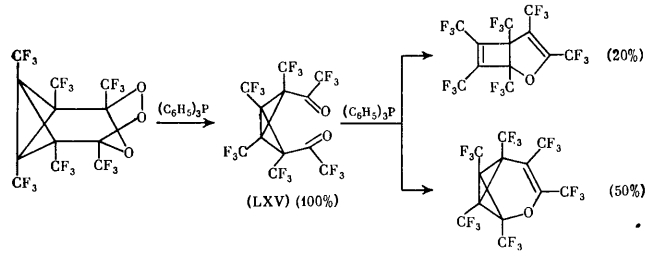


Glyoxylic acid has been used as the reductant in acetic acid[238]. Triphenylphosphine has been employed for the reduction of ozonides[239–241]. Thus the ozonides of substituted methyleneadamantantanes were converted quantitatively into adamananone after being refluxed with triphenylphosphine in hexane for 2 h.[83] The reduction of the ozonides of substituted cyclopentenes led to cyclic triacetals with the adamantane structure[26]:



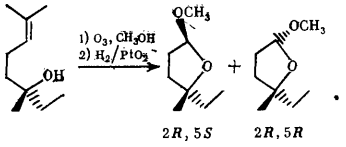
R = H or CH_3.

The ozonide of hexakis(trifluoromethyl)benzvalene has been reduced with an equimolar amount of triphenylphosphine to the diketone (LXV), which underwent further transformations in the presence of an excess of the reagent[242]:



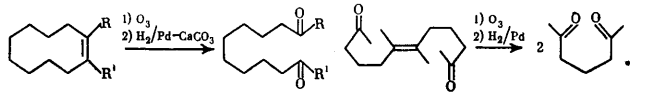
(LXV) (100%)

Methoxyhydroperoxides have been reduced electrolytically to aldehydes[243]. Selective hydrogenation on platinum group metals is a modern method[1,16,34,244–246]. Under these conditions, the product of the ozonolysis of dihydrolinalol in methanol gives rise to enantiomeric cyclic acetals, which have been separated by preparative gas–liquid chromatography[247]:

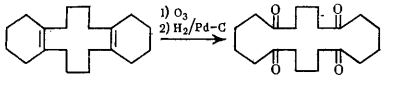


2R, 5S 2R, 5R

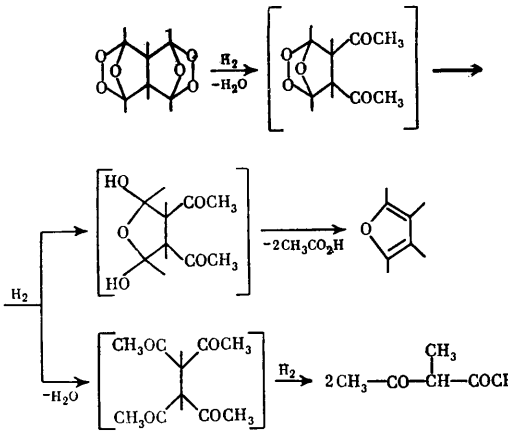
The hydrogenation of ozonides yields mainly the corresponding aldehydes, but the formation of carboxylic acids (up to 18%) as a consequence of disproportionation has also been noted[248]. If cyclohexene is ozonised in the absence of oxygen and then hydrogenated (Pd/C), then 66% of adipic dialdehyde and 24% of 5-formylvaleric acid are obtained[249]. The hydrogenation of the ozonides of substituted methyleneadamantanes results in the formation of adamantanone and the lactone (XLVIII).[83] Diketones have been obtained from cyclic[250] and linear[251] olefins with a substituted double bond:



Reductive ozonolysis has been used to synthesise macrocyclic ketones[149]:

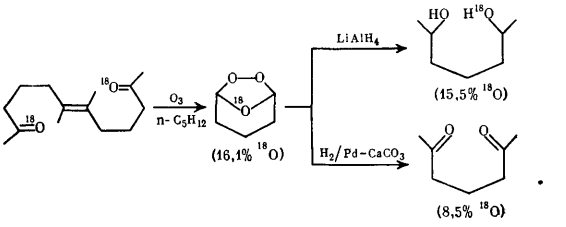


The hydrogenation of the diozonide of Dewar hexamethylbenzene led[106] to tetramethylfuran, which was identified in the form of the adduct with maleic anhydride, and to 3-methylpentane-2,4-dione:



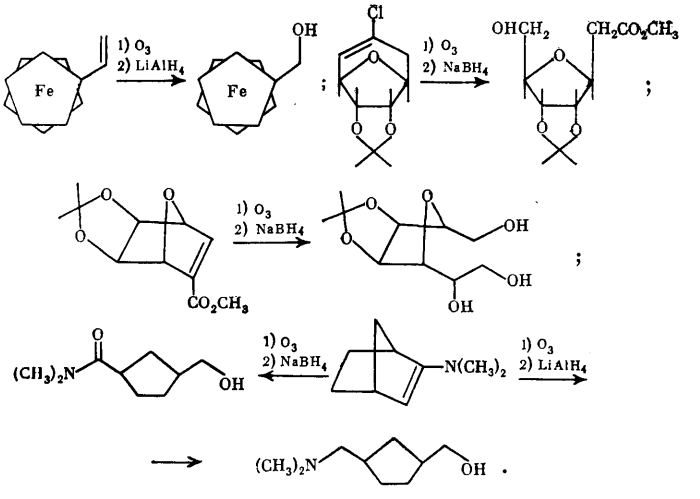
If the catalytic hydrogenation of ozonides is carried out under more severe conditions, the corresponding alcohols and glycols are obtained[252]. In the presence of amines the products are aliphatic amines[253], while diamines have been obtained from the cross-products of the ozonolysis of cycloolefins[254–256].

Complex alkali metal hydrides[1,257], boron[258], and organoaluminium compounds[259] are convenient reagents for the conversion of ozonides into alcohols. The complexes of lithium tetrahydroaluminate with chiral alcohols have reduced ozonides to optically active compounds[260]. The reaction with lithium tetrahydroaluminate takes place quantitatively with selective loss of the oxygen atom from the peroxide bridge, while in the hydrogenation over a palladium catalyst an oxygen atom is split off from both the peroxide and ether bridges[54]:



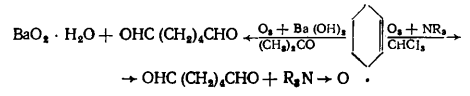
(16,1% ^{18}O) (15,5% ^{18}O) (8,5% ^{18}O)

Reductive cleavage with complex alkali metal hydrides has been used in the ozonolysis of olefinic ferrocenes[261] and in the synthesis of intermediates for nucleosides[262] and other physiologically active compounds[263]:

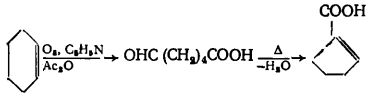


The "non-peroxide" reductive ozonolysis, carried out in the presence of compounds which take up peroxide oxygen, is of practical interest. One of the first versions was ozonolysis in the presence of tetracyanoethylene[65,264,265].

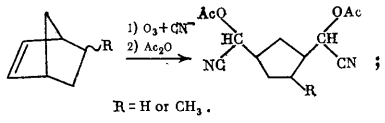
The ability of alkoxyhydroperoxides to epoxidise the double bond has been reported[266]. The reductive ozonolysis of olefins in the presence of "Baeyer–Villiger solvents" (pinacoline, cyclohexanone, and propionaldehyde)[22,23,267] was not confirmed in subsequent studies[24,27,268]. Carbonyl compounds are obtained in a single stage in ozonisation in the presence of pyridine[150], tertiary aliphatic amines[269,290], and alkaline earth metal hydroxides[271,272]:



When cyclohexene is ozonised in the presence of pyridine and acetic anhydride, then, apart from adipic acid (30%), 5-formylvaleric acid is formed (in 35–40% yield) and cyclises at an elevated temperature[273]:



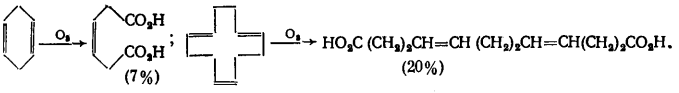
Emulsion ozonisation in the presence of reactive nucleophiles leads to non-peroxide ozonolysis products[35,274–278]. Cyano-ozonolysis has been applied to bicyclic olefins[279]:



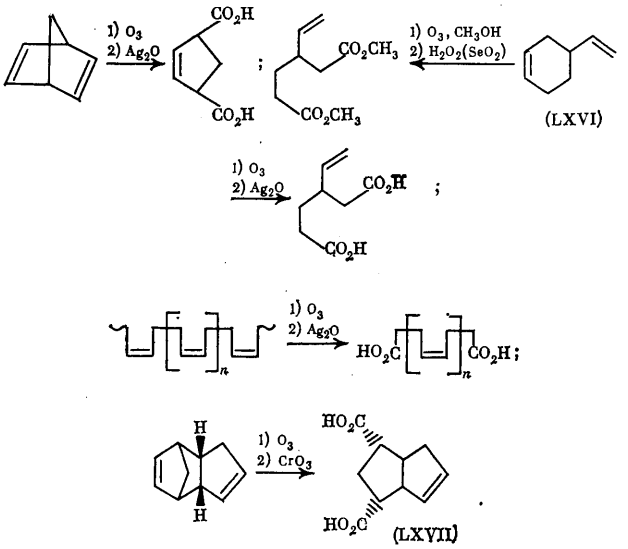
R = H or CH_3.

Methods have been developed for the determination of the positions of the double bonds in alkenes by ozonolysis and oxidation (with silver azide[280]) or reduction (with dimethyl sulphide[40,281] and triphenylphosphine[282]) and subsequent GLC analysis of the methyl esters of carboxylic acids or carbonyl compounds. The oxidative and reductive ozonolytic analytical methods have been compared[283,284]. Oxidative ozonolysis has been applied to natural rubber[285], butyl-rubber[286,287], 3-methylheptatriene–methacrylic acid copolymer[288], a mixture of isomeric bicyclic olefins[289], and natural unsaturated aliphatic acids[290]. The structures of polypiperylene[291] and isobutene oligomers[292] have been established by the ozonolysis of olefins in ethereal solvents. Reductive ozonolysis has been used to determine the structures of rubbers[293–297], poly(vinyl chloride)[298–300] and other polymers[301–303], oligomers[304], cellulose[305], and aliphatic acids[306]. The optical purities of *cis*- and *trans*-olefins have been determined with its aid[307].

Recently increasing attention has been devoted to the problem of the selectivity of chemical reactions[308,309]. In relation to the ozonolysis reaction, this problem has acquired particular importance for the specific cleavage of one of the multiple bonds in polyunsaturated compounds. Until recently, such compounds have been subjected merely to complete ozonisation in order to establish their structures. It was assumed that partial ozonolysis can be successfully achieved only when the double bonds are conjugated, whereupon the ozonide group formed exerts a significant influence on the remaining double bond, as, for example, in cyclohexa-1,3-diene[310] and *p*-divinylbenzene[11]. If the double bonds were separated by one or two carbon atoms, the unsaturated dicarboxylic acid could be obtained only in a low yield[310]:



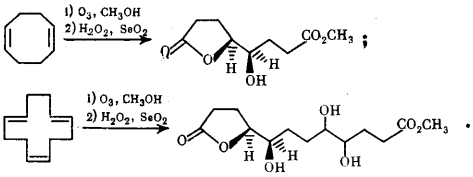
The yields of unsaturated α,ω-dicarboxylic acids increase to 50–60% in emulsion ozonisation in aqueous alkaline hydrogen peroxide[311,312]. The Asinger oxidation of the peroxy-products of the controlled ozonolysis of norbornadiene[313], 4-vinylcyclohexene (LXVI), [314–316] and poly-*cis*-buta-1,4-diene[317] led to the synthesis of the corresponding unsaturated dicarboxylic acids. The diester of 3-vinyladipic acid has been obtained by the selenium dioxide-catalysed decomposition of the peroxy-product of the partial ozonolysis of the diene (LXVI) in methanol[193,199]. Treatment of the product of the controlled ozonolysis of *endo*-dicyclopentadiene[318] with Jones' reagent yielded the acid (LXVII):



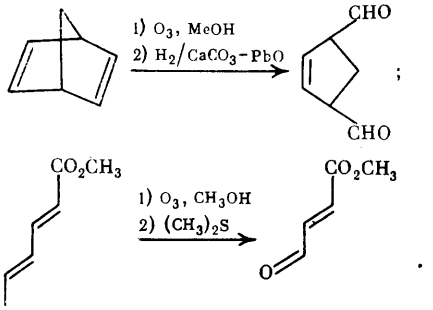
(LXVI)

(LXVII)

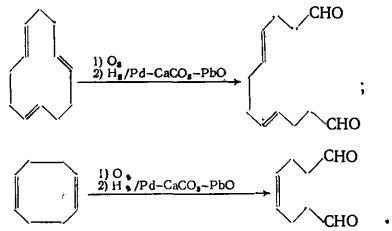
When hydrogen peroxide is used for the decomposition of the ozonides of polybutadiene[205,319,320] and polyisoprene[205,320], the hydroxylation of the double bonds results in the formation of the γ- and δ-lactones[205]. It has been shown in relation to the partial ozonolysis of the cyclic oligomers of 1,3-dienes[321,322] that this reaction is stereospecific in the presence of selenium dioxide[323]:



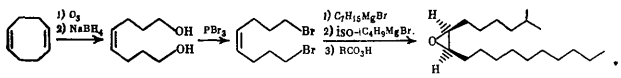
Considerable synthetic possibilities are inherent in partial reductive ozonolysis[313,324–326]:



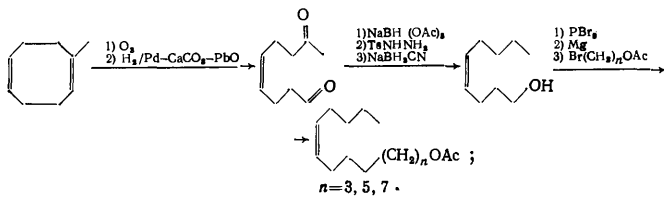
The synthesis of substances regulating the populations of insects[327–332] requires unsaturated aldehydes and ketone with a specific configuration. As a result of the selective ozonolysis of cyclic oligomers of 1,3-dienes[333], such carbonyl compounds have become available:



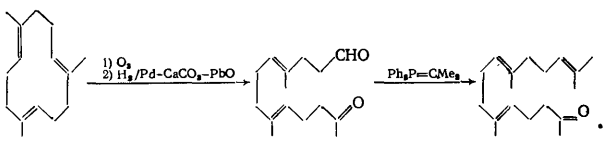
The synthesis of disparlure—the sexual attractant of the silkworm moth—has been developed on the basis of the product of selective ozonolysis of *cis,cis*-cyclo-octa-1,5-diene[334,335]:



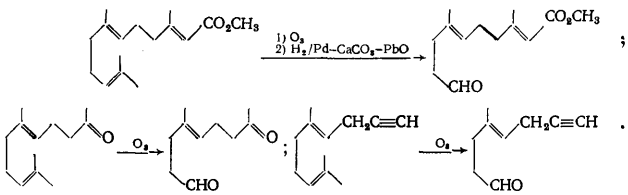
The selective cleavage of the trisubstituted double bond in 1-methyl-*cis,cis*-cyclo-octa-1,5-diene[336] constituted the basis of a new approach to the synthesis of the sexual attractants of coleoptera. These compounds have the structure of *cis*-enol acetates[330,331]:



A new stereospecific synthesis of terpenoid 1,5-polyenes involves the selective ozonolysis of cyclic isoprene oligomers[337,338]:

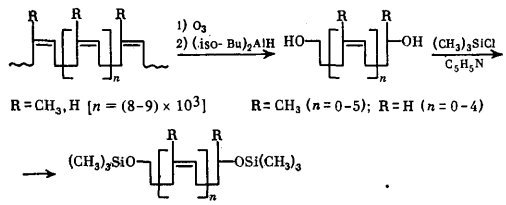


The selective ozonolysis of the isopropylidene group in linear isoprenoid compounds[339] constitutes a convenient method of synthesising regular isoprenoid blocks with terminal functional groups and double bonds having a specified configuration, which are necessary for the construction of polypropenols[340,341]:

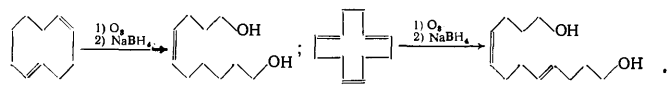


Oligomeric blocks with terminal hydroxy-groups, which have found applications as monomers, plasticisers, adhesives, coatings, and binders for rocket fuel[348], are obtained by the controlled ozonolysis of *cis*-1,4-polybutadiene[259,342,343], *cis*-1,4-polyisoprene[344,345], and copolymers of 1,3-dienes[346,347] with subsequent reduction of the ozonides.

A new approach to the synthesis of bifunctional *cis*-1,5-polyprenols[349] (from natural rubber or its synthetic analogues) and *cis*-1,5-polyenes[350] (from SKD-*cis*-1,4-polybutadiene rubber) has been developed on the basis of the selective ozonolysis of polyunsaturated rubbers with a regular structure. Individual polyenes have been isolated in the form of bis(trimethylsilyl) ethers:



When the cyclic hydrocarbon contains several double bonds of different geometry, the transoid bond is attacked preferentially[351]:



---o0o---

Thus the advances achieved in the last decade have led to the inclusion of ozonolysis among the modern methods in the chemistry of olefins. There are considerable prospects for the selective ozonolysis of cyclic and linear oligomers and co-oligomers of 1,3-dienes, which have become extremely readily available in recent years as a result of the vigorous development of the chemistry of metal complex catalysis.

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The Synthesis of Heterocycles from Vinylacetylenes or Diacetylenes and Nitrogen-containing Dinucleophiles

I.A.Maretina, A.E.Tsil'ko, and Yu.A.Zaichenko

Data on the reactivities of acetylenes substituted by conjugated electron donors or acceptors in heterocyclisation reactions with nitrogen-containing dinucleophiles are surveyed, the influence of the structure of the acetylenic component on the nature of the interaction is analysed, and the characteristics of the mode of intramolecular and intermolecular nucleophilic attack are discussed.
The bibliography includes 96 references.

CONTENTS

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I. INTRODUCTION

Acetylenic compounds are being increasingly used in reactions leading to heterocycles. Processes such as the 1,3-dipolar cycloaddition, intramolecular cyclisation, cyclisation via a double attack on the acetylenic bond, and others have come to be widely used in the chemistry of acetylenes[1]. The vigorous development of this field can be explained by the extensive possibilities, discovered in the course of research, associated with the specific reactivity of the triple bond in nucleophilic addition reactions.

The synthesis of five- and six-membered heterocycles from 1,3-bifunctional compounds containing carbonyl groups is generally known. These data have been surveyed in a series of monographs[2-4] and also in a series of reviews (see, for example, Coispeau and Elguero[5]).

Numerous studies demonstrating that in the construction of heterocyclic compounds three carbon fragments can be formed by the reactions of conjugated alkenynes or alkadiynes with dinucleophiles have been published in recent years. The mode of the intermolecular nucleophilic attack on substituted acetylenes involving mononucleophiles has been discussed in a number of monographs[1,6] and reviews[7-9].

In the present review it is shown that the participation of conjugated systems in the construction of heterocycles is a general process, but the pathways leading to the formation of rings are different when unsaturated conjugated systems and 1,3-difunctional compounds containing carbonyl groups are used. In the first place the review deals with the acid-catalysed reactions of acetylenes, substituted by conjugated electron donors, with hydrazine, hydroxylamine, and guanidine derivatives, leading to the synthesis of pyrazoles, isoxazoles, and pyrimidines. Next, the available information about the reactions of the same acetylenes under the conditions of direct nucleophilic attack, leading to pyrimidines and pyridines, is surveyed. Finally, data are presented on the reactions of dinucleophiles with acetylenes substituted by electron acceptors—ethynyl residues.

II. CYCLISATION IN ACID MEDIA WITH PARTICIPATION OF CONJUGATED ACETYLENES

The reactions of dinucleophiles with acetylenes containing conjugated donors—1-heteroalk-1-ene-3-ynes (I)—in acid media via a mechanism different from that of the cyclisation of 1,3-dicarbonyl compounds are of greatest importance in the synthesis of heterocycles. This mechanism is based on the reactions of the protonated form of the acetylenic compound.

Compounds of type (I) can undergo hydrolysis and (or) hydration in an acid medium[10-12]:

$$\underset{(I)}{RXCH{=}CHC{\equiv}CH} \rightarrow \begin{cases} \rightarrow \underset{(II)}{CHOCH_2C{\equiv}CH} \\ \rightarrow \underset{(III)}{RXCH{=}CHCOMe} \end{cases} \rightarrow \underset{(IV)}{MeCOCH_2CHO}$$

Heterocyclic systems can therefore arise in principle as a result of the interaction of the nitrogen-containing base with both the protonated form of the initial compound and with its hydrolysis or hydration products.

1. Protonation of Acetylenes Substituted by Conjugated Electron Donors

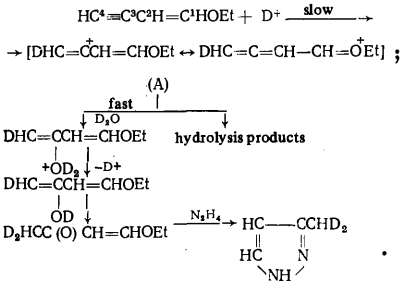
It has been shown[10,12] that the acid hydrolysis of 1-alkoxyalk-1-en-3-ynes leads to the formation of β-acetylenic aldehydes, but the authors do not present evidence for the structure of the hydrolysis products. The acid hydrolysis of the "usual" vinyl ethers[13-16] is faster by five orders of magnitude than the hydrolysis of 1-alkoxybut-1-en-3-ynes[17-19]. This fact is treated as evidence for a change in the reaction mechanism[17], total hydrolysis being preceded by the hydration of the triple bond and subsequent cleavage to acetoacetaldehyde. The mode of protonation of the conjugated system in hydrolytic reactions has been demonstrated by ^{1}H NMR [20,21] for substituted enyne ethers.

The study of the kinetics of the hydration of 1-alkoxybut-1-en-3-ynes has shown[22] that the rate of the reaction is determined by the protonation of the $C_{(4)}$ atom with formation of a conjugated carbonium ion (A), which is attacked by water molecules in the subsequent rapid stages. This is supported by the value of the isotope effect (k_{H_2O}/k_{D_2O} = 2.9); furthermore, the low entropy of activation for the hydration process (ΔS = 6.72 J mol^{-1} K^{-1} [18]) shows that in the transition state of the rate-determining stage of the process water is not firmly bound (Taft's concept[23,24]).

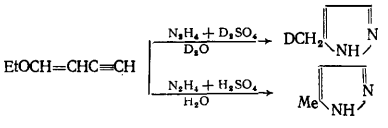
The common stage in the hydrolysis[20,21] and hydration[22] of the compounds RO–CH=CH–CH≡CR is apparently the protonation of the system at the $C_{(4)}$ atom and the formation of a mesomeric cation of type (A); the subsequent pathways in

the reaction of the cation are determined by the interaction with the electrophilic $C_{(1)}$ (hydrolysis) or $C_{(3)}$ (hydration) centre:

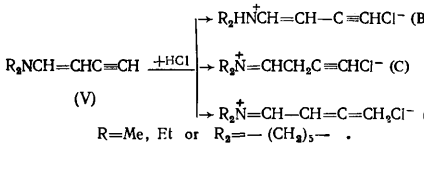
Scheme 1



When a nitrogen-containing base (hydrazine) was introduced into the reaction medium, the product of the direct interaction with the conjugated carbonium ion was isolated[22], which demonstrated the possibility of the direct cyclisation via the attack on the electrophilic centre $C_{(1)}$ or $C_{(3)}$ by a stronger nucleophile:



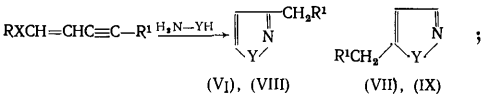
Alkynylenamines exhibit a higher reactivity in heterocyclisation reactions than the sulphur- and oxygen-containing analogues. The increased activity of the electrophilic centre at $C_{(1)}$ can be explained in this instance by the structure and properties of the protonated form produced under the cyclisation conditions[25]. Of the three possible types of salts, salt (B), which is rapidly converted via a protropic rearrangement into salt (D), is formed initially in the protonation of tertiary amines (V):



The allene structure of the immonium salts (D) has been confirmed in infrared and ultraviolet spectroscopic studies of the products of the mercuration of these amines[25]. Data[26,27] for the protonation and mercuration of enamines confirmed the immonium structure of the protonation products of amines of the vinylacetylene series. When the salt is attacked by a nucleophile, the $C_{(1)}$ reaction centre, activated by nitrogen, reacts preferentially.

2. The Reactions of the Protonated Forms of Acetylenes with Hydrazine, Hydroxylamine, and Guanidine Derivatives

The interaction of the conjugated carbonium ions examined above with bifunctional nucleophiles can take place with participation of the $C_{(1)}$ or $C_{(3)}$ reaction centre, i.e. with formation of heterocycles substituted in different ways; both possibilities are actually realised. The reactions of heteroenyne compounds with hydrazine, substituted hydrazines, and hydroxylamine, which permit inferences to be drawn concerning the reaction pathways of the conjugated carbonium ion, lead to the formation of two pyrazole isomers (VI) and (VII) or isoxazole isomers (VIII) and (IX):[28-33]



(VI), (VIII) (VII), (IX)

R^1=H, Me, Et, n-Bu, or t-Bu; Y=NR^2 (VI, VII); Y=O (VIII, IX).

The nature of the substituent X (for R^1 = H) exerts the most significant influence on the relative activities of the two reaction centres. If RX is an electron-donating substituent (an amino-,[29] an alkoxy-,[30] or an alkylthio-group[31]), for which the mesomeric effect predominates over the inductive effect at the instant of the reaction, then the reactivity is correlated with the positive mesomeric effect of the heterogroup and varies in the sequence R_2N > RO > RS.

Since in an aqueous acid medium the stage completing cyclisation is the reaction of the carbonium ion with the nucleophile[22], the structure of the final product is to a large extent determined by the activity of the $C_{(1)}$ and $C_{(3)}$ electrophilic centres in the conjugated carbonium ion. For X = NR, the electrophilic $C_{(1)}$ centre exerts the greatest influence and the main products are the isomers (VII) and (IX).[29] For X=O, there is competition between the electrophilic $C_{(1)}$ and $C_{(3)}$ centres, the role of the latter centre increasing on passing from oxygen to sulphur-containing derivatives in conformity with the decrease of the +*M* effect in this sequence[30].

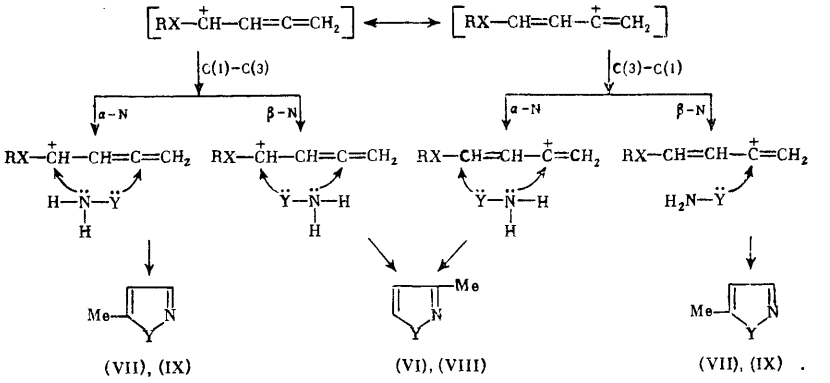
The influence of the nature of the substituents at the acetylenic linkage (R^1) is not manifested to quite such an extent. Substitution reduces the activity of the $C_{(3)}$ centre as a result of polarisation effects and steric factors; this increases the amount of 5-substituted pyrazoles or isoxazoles[33]. The influence of substitution at the acetylenic bond can be analysed from data for the synthesis of isoxazoles by the interaction of the homologues of 1-methoxybut-1-en-3-yne with hydroxylamine[30]. The amount of isomer (IX) increases in the homologous series.

On the other hand, the nitrogen-containing dinucleophiles H_2N=YH (Y = O, NH, NA, or NMe) can react with the $C_{(1)}$ electrophilic centre of the carbonium ion via two alternative pathways: (1) attack on the α-nitrogen atom [the formation of isomers (VII) and (IX)]; (2) attack on the β-atom (oxygen or nitrogen) [the formation of isomers (VI) and (VIII); see Scheme 2].

For H_2NOH, the sharp difference between the nucleophilic properties of the two centres of the base (nitrogen and oxygen) improves the picture—the primary amino-group reacts with the $C_{(1)}$ centre of the carbonium ion [$C_{(1)}$–$C_{(3)}$ α-N-attack, isomer (IX)]. Such data have been obtained for X = NR; the reaction of 1-dialkylaminoalk-1-en-3-ynes with hydroxylamine leads to the specific synthesis of 5-alkylisoxazoles[29]. In view of the foregoing, one must emphasise the comparative value of the method, because the use of dicarbonyl compounds as starting materials results in a mixture of 3- and 5-alkylisoxazoles[3].

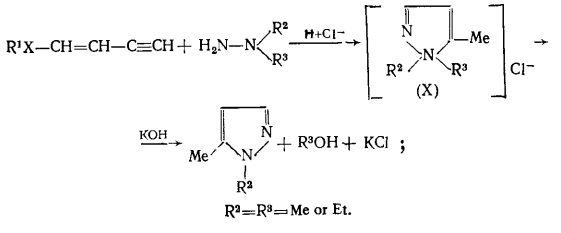
A comparative estimate has been made of the reactivities of the two-centres (α- and β-) of asymmetric hydrazines[33]. In monoalkylhydrazines the substituted nitrogen atom is more nucleophilic and it is therefore logical to postulate the possibility of β-N-attack on the electrophilic $C_{(1)}$ centre. However, in the reaction of 1-dialkylaminobut-1-en-3-ynes with methylhydrazine only between 5 and 15% of isomer (VI) is formed as a result of an attack of this type ($C_{(1)}$–$C_{(3)}$),

Scheme 2



β-N).[29] In $H_2N-NHAr$ the nucleophilic activity of α-N is higher than that of β-N, so that attack on the electrophilic $C_{(1)}$ and $C_{(3)}$ centres by the α-nitrogen atom of phenylhydrazine predominates for X = NR, O, or S.

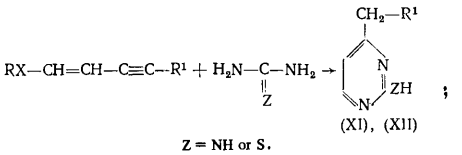
Asymmetric dialkylhydrazines $H_2NNR^2R^3$ reacted anomalously with enyne amines, ethers, and sulphides (X = NR, O, or S)[33]—the $C_{(1)}$ centre was attacked exclusively by the less nucleophilic α-nitrogen atom. The cause of the anomaly is apparently steric hindrance. Cyclisation led to the formation of quaternary pyrazolinium salts (X), which underwent the Hofmann degradation under the influence of concentrated alkali with formation of 1,5-dialkylpyrazoles (20%) and also the aminonitrile rearrangement[34]:



$R^3 = R^3 = Me$ or Et.

With the exception of asymmetric dialkylhalides, the nitrogen-containing bases examined exhibit the α-effect in nucleophilic addition reactions involving the carbonyl group and in nucleophilic substitution reactions[36].

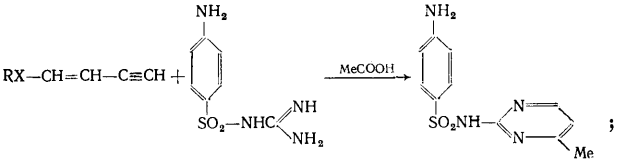
The reaction of a carbonium ion with nucleophiles such as guanidine and its derivatives leads to the formation of pyrimidine bases. Alk-1-en-3-ynyl ethers and sulphides react with guanidine or thiourea in an acid medium to give 4-alkyl-2-aminopyrimidines or 4-alkyl-2-mercaptopyrimidines [compounds (XI) and (XII)]:[37-39]



Z = NH or S.

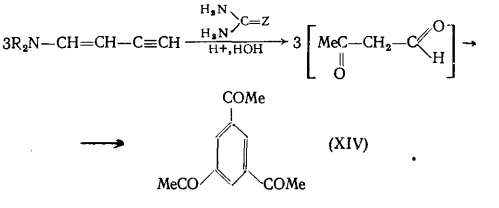
2-Amino-4-methylpyrimidine is used in the synthesis of pharmaceutical preparations[41]. Pyrimidinethiols accelerate the vulcanisation of rubbers[40].

The synthesis of sulfamerazine [2-(*p*-aminobenzenesulphonamido)-4-methylpyrimidine (XIII)], a long-action sulphonamide preparation, by the reaction of 1-heterobut-1-en-3-yne with 2-*p*-aminobenzenesulphonylguanidine is also of practical interest[42]:



RX = Et_2N, EtS, or EtO.

When 1-dialkylaminobut-1-en-3-yne is condensed with guanidine or thiourea in an acid medium, pyrimidine derivatives are not formed[37]. Only triacetylbenzene (XIV)—the product of the trimerisation of acetoacetaldehyde—was isolated from the reaction mixture. Thus, the reactions of a carbonium ion with water (hydrolysis, hydration, and trimerisation) are faster than the interaction with the nitrogen-containing base, which leads to pyrimidines:

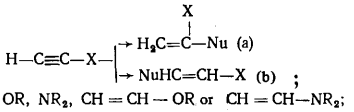


The results show that, among the three parameters (basicity, polarisability, and α-effect) characterising the reactivity of the nitrogen-containing base, the last factor apparently plays a significant role.

Evidently in an aqueous acid medium hydrolysis and hydration are not obligatory intermediate stages in the reaction with nitrogen-containing dinucleophiles. This view is based on the experiments, discussed above, using labelled atoms as well as data for the reactions of 1-dialkylaminobut-1-en-3-ynes with guanidine in an acid medium, which show that in the course of the reaction the hydrolysis and hydration products do not interact with nitrogen-containing dinucleophiles.

III. THE HETEROCYCLISATION OF ACETYLENES SUBSTITUTED BY CONJUGATED ELECTRON DONORS UNDER THE CONDITIONS OF DIRECT NUCLEOPHILIC ATTACK

The mode of intermolecular addition of nucleophiles to acetylenes of the type H–C≡C–X is determined by the nature of the donor X:

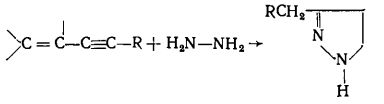


(a) X = OR, NR_2, CH = CH – OR or CH = CH–NR_2;
(b) X = SR or CH = CH – SR .

Thus, under the conditions of intermolecular attack, the nucleophile enters the α-position in alkynyl ethers (X = OR), enynyl ether (X = CH=CH–OR), and their nitrogen-containing analogues (X = NR_2 or CH=CH–NR_2) and the β-position in ethynyl sulphide (X = SR) or enynyl sulphide (X = CH=CH–SR).[45] This difference in the mode of addition is associated with the nature of the donor. The main factor responsible for the difference between the chemistry of sulphur, on the one hand, and that of oxygen and nitrogen, on the other, is the presence of *d* orbitals and the capacity for π–*d* interaction. These features are responsible for the attack on the β-carbon atom[46].

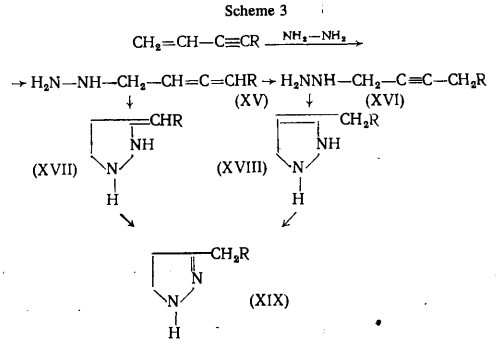
In cyclisation reactions the configuration of heterosubstituted enynes of all three types is the same ($C_{(1)}$–$C_{(3)}$ or $C_{(3)}$–$C_{(1)}$). The most varied heterocyclic compounds can be obtained from acetylene derivatives substituted by conjugated electron donors or nucleophiles capable of adding to a triple bond.

The only instance of the interaction of vinylacetylenic systems with hydrazine known in the literature refers to the synthesis of pyrazolines[47]:

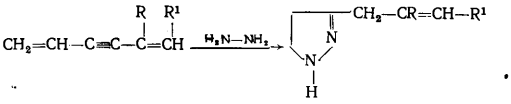


The authors[47] suggest that hydrazine adds in the 4,1-positions with subsequent cyclisation of the intermediate allene derivatives (XV) and the acetylene derivatives of hydrazines (XVI) to the unstable heterocycles (XVII) and (XVIII), which isomerise irreversibly to stable final 2-pyrazolines (XIX):[48]

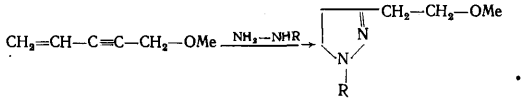
Scheme 3



In the reactions with mono- and di-substituted homologues of divinylacetylene hydrazine adds to the 4,6-positions with formation of 3-allylpyrazolines:

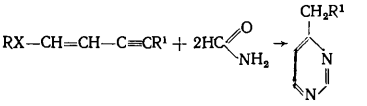


Hydrazine adds to the triple bond of isopropenylethynylmethanol[49]. Enynyl ethers with a non-conjugated alkoxy-group combine with monosubstituted hydrazines in the 1,3-positions[50]:

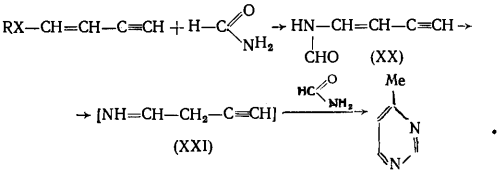


If the three-carbon fragment consists of a 1,3-conjugated enyne system, while the nitrogen-containing fragment is an amidine, thiourea, urea, guanidine, or formamide, the reaction products are pyrimidine derivatives.

4-Alkylpyrimidines have been obtained by the reaction of 1-heteroalk-1-en-3-ynes with formamide:[39, 51]

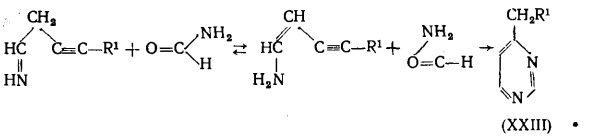


The reaction of alk-1-en-3-ynes probably proceeds via the nucleophilic substitution of the hetero-group by the amino-group of formamide with formation of the formamido-compound (XX) and the imine (XXI):



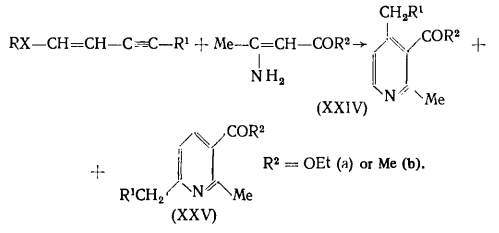
Such transamination has been proved by the isolation of dialkylformamides in the reaction with 1-dialkylaminobut-1-en-3-ynes[39]. The substitution of the stronger nucleophile (the dialkylamino-group) by the amino-group of formamide is possible according to the Law of Mass Action—when a tenfold excess of formamide is introduced into the reaction.

The formamido-compound (XX) is decarbonylated to the imine (XXI). Although the latter could not be detected, examples of stable compounds (XXII) of this kind have been described in the literature; they have been obtained by the reaction of formamide with benzoylacetone and were subsequently converted into pyrimidines at 220 °C.[52] The iminoketone is a proven intermediate in Bredereck's pyrimidine syntheses[53–56]. The imine (XXII) reacts with a second formamide molecule to form the pyrimidine ring (XXIII):



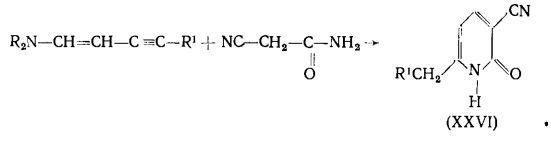
In the synthesis of pyridine systems, 1-dialkylamino(1-alkoxy)alk-1-en-3-ynes can be used as the three-carbon donors[57,58]. The two-carbon fragment can be supplied by enamines (for example, ethyl β-aminocrotonate), acetylacetone imine[57,58], and cyanoacetamide[29]. The main reaction

products are respectively ethyl 4-alkyl-2-methylnicotinate (XXIVa) and 3-acetyl-4-alkyl-2-methylpyrimidines (XXIVb) (90%, gas–liquid chromatographic method):



The proportions of the isomeric esters of 2,4-dimethyl- and 2,6-dimethylnicotinic acids (XXIVa) and (XXVa) have been determined chromatographically and by ^{1}H NMR, the two methods yielding satisfactorily concordant results[58].

Alk-1-en-3-ynylamines[29] condense with cyanoacetamide to form 6-alkyl-3-cyano-2-pyridones (XXVI):



The reactions described above are of interest in the sense that the involvement of the medium is ruled out—the interaction occurs on direct mixing of the reactants.

The formation of two isomers in the reactions of alk-1-en-3-ynes and alka-1,3-dienes with enamines (ethyl β-aminocrotonate or acetylacetone imine) can be accounted for by the ability of the two electrophilic centres of the initial 1,3-bifunctional compound and the two nucleophilic centres of the imine to compete.

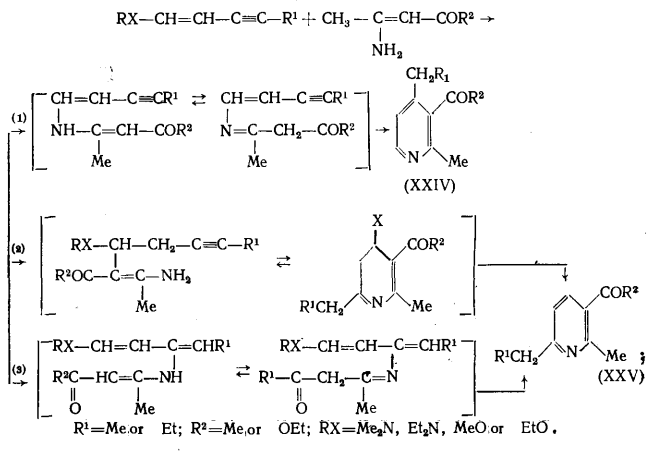
The above systems can interact with enamines in three ways.

1. Via the transamination of the hetero-group with participation of the $C_{(1)}$ reaction centre and intramolecular cyclisation involving the active methylene group and the C≡C triple bond: this results in the formation of the 2,4-isomer (XXIV).

2. By the Michael addition of the active methylene group to the C=C double bond and subsequent intramolecular cyclisation via NH attack [the formation of the 2,6-isomer (XXV)].

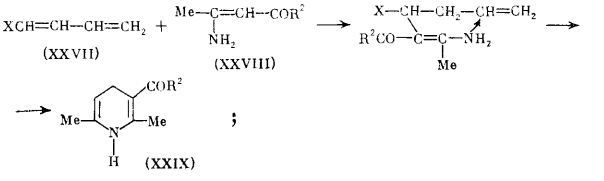
3. Via the nucleophilic attack by the primary amino-group on the $C_{(3)}$ reaction centre of the 1,3-enyne and cyclisation via the Michael addition involving the electrophilic $C_{(1)}$ centre of the conjugated system [the formation of the 2,6-isomer (XXV); see Scheme 4].

Scheme 4



Pathway (1) involves the initial addition of the primary amino-group to the electrophilic $C_{(1)}$ centre, which has a reduced electron density. This nature of the reaction presupposes the involvement of the free amino-group. Indeed, the stable *cis*-enamine structure of enaminoketones and enaminoethers unsubstituted at the nitrogen atom, stabilised by a hydrogen bond between the amino-nitrogen and the carbonyl oxygen, has been demonstrated in a number of studies[59–61].

Pathway (2) operates in the interaction of dienylamines with enaminoketones and enaminoethers with formation of isomers (XXIX) [58] (yield 10%):



Pathway (3) can apparently occur only for 1,3-substituted enynes, because there are data indicating the nucleophilic attack on the triple bond of hetero-substituted 1,3-enynes by primary amines[45]. The reactivities of the electrophilic $C_{(1)}$ and $C_{(3)}$ centres in alkoxyenynes in a neutral medium are comparable, which can account for the formation of up to 50% of the product resulting from the attack by the amino-group on the triple bond.

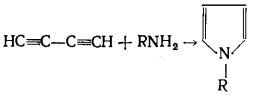
IV. THE REACTIONS OF ACETYLENES SUBSTITUTED BY CONJUGATED ELECTRON ACCEPTORS IN REACTIONS WITH MONO- AND DI-NUCLEOPHILES

Reactions involving the addition of primary and secondary amines of all types to triple bonds conjugated with activating groups of different kinds have been described in the literature[6,62].

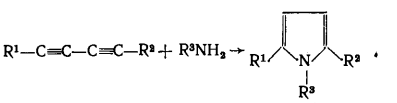
Thus the addition of primary amines to a diacetylene leads immediately to a 1 : 2 adduct[63], which undergoes the enamine—imine prototropic rearrangement[45,64]. Methyldiacetylene reacts with primary amines only at the unsubstituted acetylenic bond[65].

Secondary amines add to the 1,2-positions contrary to the Markovnikov rule[66–69]. Monoalkyldiacetylenes combine with secondary amines only at the terminal acetylenic bond[70]. Secondary amines add in the same manner to diacetylenic alcohols[71].

If the reaction of diacetylene with ammonia and primary amines is carried out in the presence of copper chloride, the products are pyrrole and its derivatives[72]:

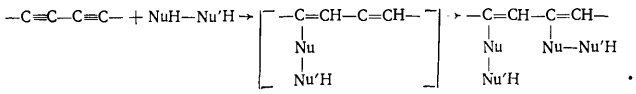


The reaction involving disubstituted symmetrical diacetylenes yielded 1,2,5-tri-substituted pyrroles[73,74]:



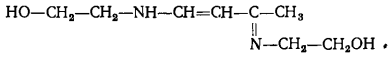
In this reaction the role of the catalyst consists in the formation of a non-polar π-complex with the triple bond, in which the electron density is uniformly distributed over both carbon atoms[75], which facilitates the closure of the pyrrole ring on interaction of the nucleophilic nitrogen with the fourth atom of the conjugated system.

The interaction of nitrogen-containing dinucleophiles with alka-1,3-diynes can proceed via two pathways—with formation of linear or cyclic structures. The mode of reactions of the first type resembles that of the reaction of diacetylene with mononucleophiles:

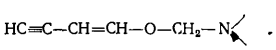


When there are two reaction centres of different strengths in the nucleophile, the centre with the maximum electron density reacts.

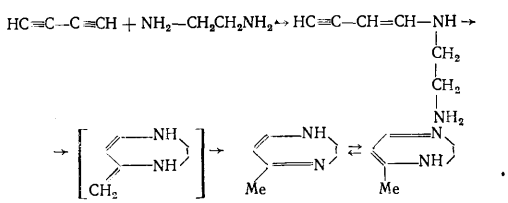
Thus, monoethanolamine adds to diacetylene as a primary amine, forming an adduct with a linear structure[76], which undergoes a prototropic transformation with fixation of the aminovinyl ketimine structure:



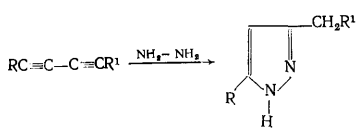
Aminoalcohols containing a disubstituted amino-group react with diacetylene to form adducts with a linear structure[77,78];



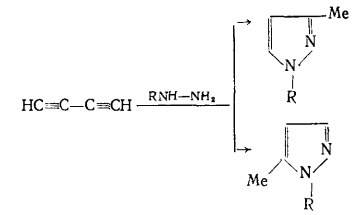
Aliphatic and aromatic diamines readily react with diacetylene, forming cyclic monoadducts. A seven-membered ring, corresponding to 1,3-addition, has been obtained from ethylenediamine[79]. Propylene-1,2-diamine adds to diacetylene in the same way[80].



Three groups of workers published comparatively recently [45,81,82] data concerning the possibility of synthesising pyrazole derivatives from diacetylene and its mono- and di-substituted homologues:

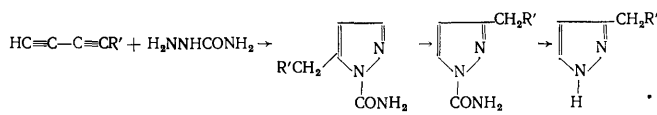


The remarks of different investigators concerning the mode of addition are inconsistent. Thus, when methyldiacetylene $HC^1{\equiv}C^2{-}C^3{\equiv}C^4{-}Me$ condenses with hydrazine hydrate[49], 3,5-dimethylpyrazole is formed together with 3(4)-ethylpyrazole, which confirms the possibility of a mixed attack on the conjugated diyne system in both the 1,3-positions and the 4,2-positions in proportions of 6 : 1. Furthermore, a study of the reaction of diacetylene with monosubstituted hydrazines[47] showed that in the absence of water the reaction leads to the formation of the 1,3-isomer, while in the presence of water the 1,5-disubstituted pyrazoles are obtained:[47,83]

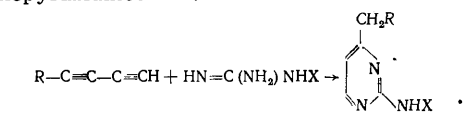


According to other data[84], the reaction of diacetylene with methylhydrazine in an alcoholic medium in the presence of sodium alkoxide leads to the formation of a mixture of isomeric 1,5- and 1,3-dimethylpyrazoles in proportions of 4 : 1.

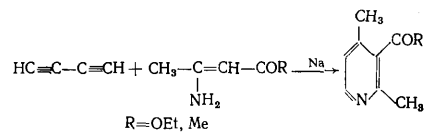
The amides of 5-alkylpyrazole-1-carboxylic acids, corresponding to the 1,3-mode of attack on the conjugated diyne system, have been obtained by the reaction of buta-1,3-diene and its asymmetric homologues (penta-1,3-diyne and hexa-1,3-diyne) with semicarbazide[85]; under the reaction conditions, the amides isomerise irreversibly to the amides of 3-alkylpyrazole-1-carboxylic acids according to literature data:



It has been established that diacetylene and its monosubstituted homologues react with guanidine or dicyanodiamide in the presence of equimolar amounts of sodium methoxide with formation of 4-alkyl-2-aminopyrimidines or 4-alkyl-2-cyanaminopyrimidines[86,87]:



The condensation of diacetylene with ethyl β-aminocrotonate or acetylacetone imine in the presence of equimolar amounts of metallic sodium results in the formation of ethyl 2,4-dimethylnicotinate or 3-acetyl-2,4-dimethylpyrimidine[88]:



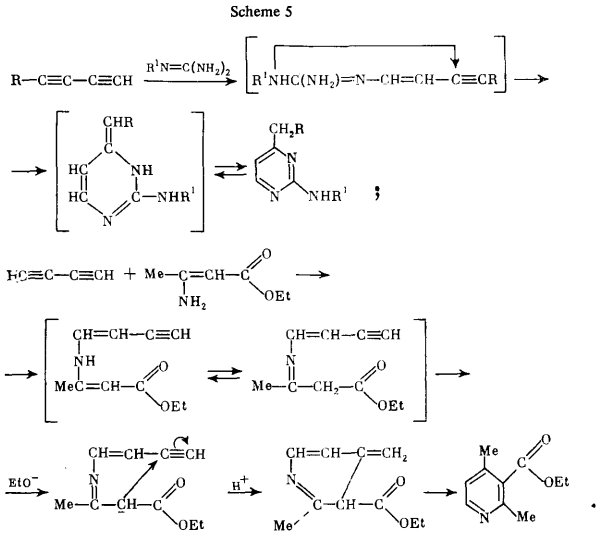
It is known that acetylenic residues have an electronegativity of the same order of magnitude as cyano-groups and a higher electronegativity than the carboxy- or carbonyl group[89]. In systems where the triple bond is conjugated with electron-accepting groups, which enhance the electron deficiency at the $C_{(4)}$ atom, the attack by the nucleophile is therefore directed to the terminal carbon atom of the triple bond.

In the $C{\equiv}C{-}C{=}O$ system, which has two electrophilic centres of different hardness, one-centre nucleophiles (alcohols, amines, CH-acids) add in the 4,3-positions. Two-centre nucleophiles such as hydrazine and semicarbazide (much stronger bases) add in the 1,2-positions, i.e. they attack the electrophilic carbon atom of the carbonyl group. Hydroxylamine (a weaker nucleophile than semicarbazide) reacts via both centres[90]. If the electron acceptor at the $C_{(1)}$ atom is "strengthened", the reaction of the system with hydrazine proceeds via the same mechanism as with amines. For example, the esters of ethyleneglyoxalic acid react with alkylhydrazines[90] via the triple bond (4,3-order of addition). The reaction of the nitriles of acids of the enyne series with hydrazine takes place in the $C_{(2)}{-}C_{(4)}$ positions. Hydrazine,

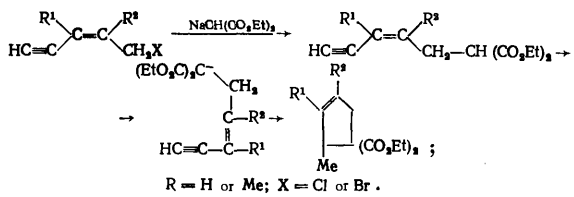
alkylhydrazines, and phenylhydrazine[91] add to these nitriles at the triple bond with subsequent cyclisation via the double bond and the formation of pyrazolines with a non-conjugated cyano-group in the side chain.

In the formation of six-membered rings, cyclisation takes place via the NH attack (pyrimidines) or CH attack (pyridines):

Scheme 5



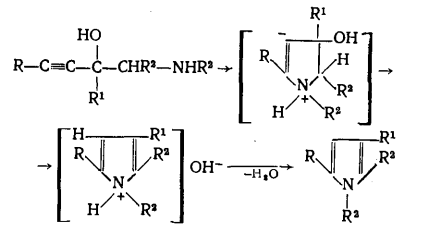
An example of the intramolecular CH attack on the acetylenic bond has been published[92]. The condensation of *cis*-1-chloropent-2-en-4-yne with sodiomalonic ester results in the formation of the diester of substituted 2-methyl-3-cyclopentene-1,1-dicarboxylic acid; the cyclisation takes place as the result of the interaction of the carbanion with the electrophilic centre of the triple bond:



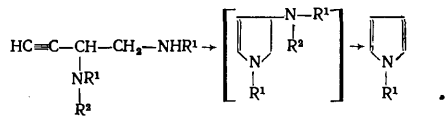
R = H or Me; X = Cl or Br.

Numerous examples of the intramolecular N–H addition to acetylenic bonds, leading to the formation of cyclic compounds, have been described in the literature. A thorough review[91] devoted to the intramolecular cyclisation of various types of acetylenic amines has been published recently. A significant factor in the formation of pyridine and pyrimidine derivatives is the tendency towards the formation of an energetically stable aromatic system. Thus the addition of primary amines to acetylene homologues[65] requires high temperatures and proceeds with much more difficulty than the reactions of the same homologues with guanidine and dicyanodiamide.

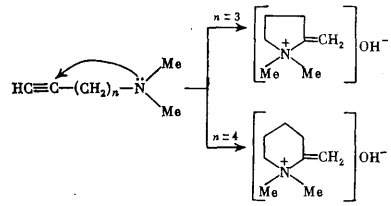
The nature of the reactions of acetylene derivatives containing the amino-group in a position non-conjugated with the multiple bond differs from that of the reactions just examined. α-Hydroxyethynyl alcohols react with primary amines to form β-aminoethynyl alcohols, which are converted into pyrroles on heating; the electron pair of the nitrogen atom then attacks the electrophilic centre of the triple bond and the resulting dipolar ion is stabilised by the simultaneous liberation of water and the migration of hydrogen[91]:



The intramolecular cyclisation of acetylenic diamines proceeds via the same mechanism but under more severe conditions, as a consequence of the reduced electrophilic properties of the triple bond[93]:

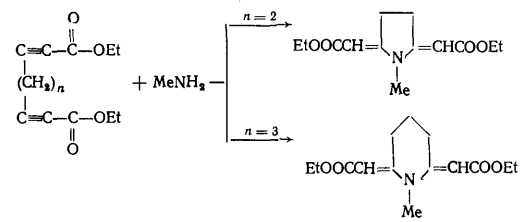


The tendency towards aromatisation apparently promotes the occurrence of these reactions, because tertiary acetylenic amines[94] cyclise at the second carbon atom. For $n = 2$, the reaction does not occur and for $n = 3$ or 4 quaternary ammonium bases derived from α-methylenepyrrolidine or α-methylenepiperidine are formed:

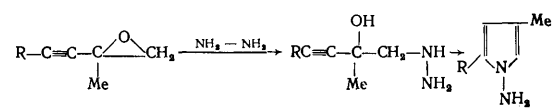


Here the nature of the attack on the acetylenic bond is different than in the examples quoted above[91,93] and corresponds to the polarisation of the acetylenic bond.

The double addition of primary amines to a non-conjugated diacetylenic system in the reaction of methylamine with esters of hexa-1,5-diyne-1,5-dicarboxylic or hepta-1,6-diyne-1,6-dicarboxylic acid is of interest[95]:



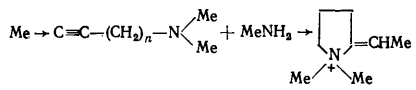
When hydrazine reacts with acetylenic epoxides, the resulting hydrazinoalcohols cyclise to five-membered heterocycles with elimination of the functional group and aromatisation of the system[96]:



In this case there is a possibility, in principle, of the formation of both five-membered and six-membered rings. However, only a five membered ring is obtained, because in the

transition state the reaction centres are in closer proximity on formation of five-membered rings.

The influence of the nature of substituents at the triple bond is pronounced in the absence of a conjugated bond system. Thus, in the series of tertiary acetylenic amines the replacement of hydrogen by an alkyl group makes the formation of five-membered rings difficult and six-membered rings are not formed at all:



The replacement of hydrogen by an alkyl group lowers the rate of the reaction but does not alter its general character.

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The data presented in this review show that electronic factors exert a decisive influence on the reactivity of the acetylenic bond in the reactions of the types considered. If the triple bond is conjugated with an electron donor, the attack by the nucleophile is directed to the α-carbon atom, while in conjugation to an electron acceptor the β-carbon atom is attacked.

The pathways leading to the formation of rings—the usual pathway (based on 1,3-dicarbonyl compounds) and the pathway described here (based on 1,3-conjugated systems)—have different mechanisms. In the first instance there is a two-stage process (for example, pyrazoles and pyrazolines are formed by hydrazones), while in the second instance both centres participate in the reaction, apparently synchronously, via a many-centre mechanism. The reactions described, based on unsaturated conjugated systems or bifunctional compounds, differ also in their results—isomers of different structures are formed; whereas the reactions with β-dicarbonyl compounds give rise to mixtures of isomers, in the second case there is a specific synthesis of only one of the two possible products.

The heterofunctional derivatives of vinylacetylene investigated do not enter into intermolecular reactions with many nucleophiles and do not combine with weak CH acids, while the cyclisation with participation of such substances takes place readily. Thus transformations which do not occur in intermolecular reactions do take place in cyclisation, the decisive factor being the tendency of the system towards aromatisation.

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The 1,5-Shift Reaction

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Data on the reaction involving the 1,5-shift of hydrogen and substituents in cyclic and acyclic dienes and trienes as well as homodienyl systems published up to June 1979 are considered and treated systematically.
The bibliography includes 197 references.

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I. INTRODUCTION

Since the discovery in 1961 of the 1,5-hydrogen shift reaction[1], isomeric transformations of diene and polyene hydrocarbons have attracted much attention by investigators. Without exaggerating, one may say that studies in this field as well as investigation of other types of thermal intramolecular rearrangements have now become an independent and vigorously developing branch of organic chemistry. Studies in this field are important for the understanding of the general problem of valence tautomerism and valence isomerisation.

In the series of the so-called sigmatropic rearrangements the 1,5-shift of hydrogen and substituents is now the most thoroughly investigated reaction, but there is no review literature of any kind on this problem. The aim of the present review is to fill this gap. The available literature data are classified in terms of different types of hydrocarbon systems; the arrangement of the material corresponds approximately to the chronology of its publication.

The series of cyclopentadienes is historically the first and most thoroughly investigated system in which the 1,5-shift of both hydrogen and substituents has been observed.

II. CYCLOPENTADIENES

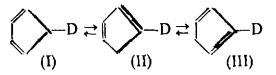
1. The Hydrogen 1,5-Shift

Inspection of early literature data shows that in many instances where the structure of the substituted cyclopentadiene had been sufficiently reliably established the distribution of double bonds in the substance was inconsistent with the expectation based on the synthetic scheme. Thus the decarboxylation of 2,4-diphenylcyclopenta-1,3-diene-1-carboxylic acid[2] yielded 1,4-diphenylcyclopentadiene instead of the expected 1,3-isomer. The cyclopentadienecarboxylic acid formed when cyclopentadienylpotassium is treated with carbon dioxide is the 1-isomer[3] and not the 5-isomer postulated previously. The dehydration of 2,3,4-trimethylcyclopent-2-en-1-ol leads to 1,2,3-trimethylcyclopentadiene instead of the 1,2,5-substituted compound[4]. Methyl cyclopenta-1,3-diene-1-carboxylate reacts partly in the form of the 2-isomer on dimerisation[5-7]. The pyrolysis of 3,3-dichlorocyclopent-1-ene leads to 2-chlorocyclopentadiene and not to the corresponding 1-isomer[8]. Finally, the dehydration of 1-phenylcyclopenta-2-en-1-ol yielded 1-phenylcyclopentadiene instead of 2-phenylcyclopentadiene[9]. Anomalous phenomena have also been observed in the alkylation of sodium, lithium, and magnesium derivatives of the cyclopentadienyl anion. Examination of the mechanism of the above reactions shows that the addition of a substituent to any of the equivalent carbon atoms of the cyclopentadienyl anion should result in the formation of 5-substituted cyclopentadiene. However, in reality the reaction usually gave rise to a mixture of the 1- and 2-isomers,[10-13] while under milder conditions the main products were the 1-isomers[12,14,15].

The independence of the structure of the substituted cyclopentadiene of the method of synthesis has been demonstrated by Mironov and coworkers[16,17], who established that five different synthetic pathways, formally designed to produce 1,4- or 2,5-dimethylcyclopentadienes, in all cases yield only 1,3-dimethylcyclopentadiene. The authors, who had previously observed the above anomalies, either did not attempt to explain them or explained them by the irreversible isomerisation of the substituted cyclopentadiene, formed initially, to the energetically more favourable isomer. The majority of investigators were convinced that the endocyclic double bonds in the cyclopentadiene ring are rigorously fixed; furthermore, the absence of isomerisation of cyclopentadienes was believed to have been proved[18,19].

In 1961 Mironov and coworkers[20-26] demonstrated that the system of double bonds in the cyclopentadiene ring exhibits an exceptionally high mobility. Special low-temperature methods of synthesis of cyclopentadienes were developed, which made it possible to obtain the individual isomers and

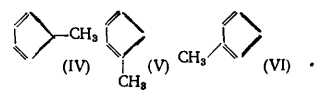
to investigate their thermal transformations. Direct interconversions of the isomeric cyclopentadienes were observed for the first time[20] in relation to 5-deuterocyclopentadiene (I) synthesised by treating cyclopentadienylmagnesium bromide with deuterium oxide at −5 °C. In the course of 1 h at 60 °C the diene (I) was converted into a mixture of equal amounts of 5-, 1-, and 2-deuterocyclopentadienes (I), (II), and (III), the transformation not being accompanied by hydrogen exchange between the molecules[20,26]:



(I) (II) (III)

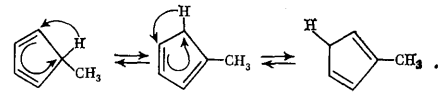
Mironov and coworkers[20,26] explained this process by the irreversible migration of the double bond system with a simultaneous shift of the hydrogen atom from the 5-position of the cyclopentadiene ring, which leads to the establishment of thermodynamic equilibrium involving isomers (I)–(III). In structure (I) a shift of the double bonds is also possible as a result of the analogous migration of the deuterium atom, although such rearrangement is degenerate, since it does not alter the structure of the substance. The measurement of the infrared spectra of diene (I) at successive time intervals during the attainment of the given equilibrium showed[26,27] that the deuterocyclopentadienes isomerise in the following sequence (I) ⇌ (II) ⇌ (III).

Low-temperature methods of synthesis of all three possible isomers of methylcyclopentadiene, namely (IV), (V), and (VI), have been described[22,23]:



(IV) (V) (VI)

It has been established[22,23,26] that at 298 K in the liquid and gas phases 5-methylcyclopentadiene (IV) isomerises to the 1-substituted diene (V). The reaction is virtually completed after 3 h in the liquid phase and after 4 h in the gas phase; 2-methylcyclopentadiene (VI) is then formed only in insignificant amounts (<5%). It has been noted that the concentration of isomer (IV) decreases by a factor of two after equal time intervals (the reaction half-life is constant). The diene (V) isomerises much more slowly but after 2–3 days at 25 °C in the liquid phase (and even more slowly in the gas phase) the substance is transformed into a mixture of approximately equal amounts of the 1-substituted isomer (V) and the 2-substituted isomer (VI) containing <3% of isomer (IV); subsequently the mixture composition no longer changes. Distillation of dienes (IV), (V), or (VI) at atmospheric pressure[22,23,26] (b.p. ~72 °C) leads to the formation of the same mixture of dienes (V) and (VI). The formation on thermal isomerisation of each methylcyclopentadiene of the same mixture, which subsequently does not change, enabled the authors[22,23,26] to conclude that thermodynamic equilibrium is established between the dienes. The formation of homogeneous 1-methylcyclopentadiene (V) at intermediate stages of the transformation of 5-methylcyclopentadiene into a mixture of dienes (V) and (VI) shows that, in the course of equilibration and evidently also in the state of equilibrium, the double bonds migrate selectively via a mechanism corresponding to the migration of hydrogen from the 5-position of the cyclopentadiene ring to a neighbouring carbon atom or via a 1,5-hydrogen shift mechanism†:



(IV) (V) (VI).

Analogous series of experiments were carried out by the same workers in relation to 1,2-dimethyl-,[25] 1,2,3-trimethyl-,[24] and 1,2,3,4-tetramethyl-substituted[21] cyclopentadienes. In each of the instances mentioned above the dienes were found to isomerise readily, the process being completed by the attainment of thermodynamic equilibrium between isomers differing in the position of the system of endocyclic double bonds. The sequence of the interconversions of the isomers, corresponding to the 1,5-hydrogen shift mechanism, has also been observed[24].

The experimental data described enabled the authors[26] to reach the following conclusions. At a relatively low temperature (20–80 °C) the system of endocyclic double bonds in the cyclopentadiene ring migrates and the reaction results in the formation of equilibrium mixtures of isomers. The interconversions of the isomeric cyclopentadienes take place rigorously selectively as a result of the migration of hydrogen from the 5-position in the cyclopentadiene ring to a neighbouring carbon atom (in the 1-position), which is consistent with the 1,5-hydrogen shift mechanism. The reaction proceeds via an intermolecular mechanism, since it is not accompanied by hydrogen exchange between the molecules and is of first order (the half-life of the reaction is constant and the rates of isomerisation in the liquid and gas phases are comparable).

By using procedures analogous to those of Mironov and coworkers[20,26], Roth[28] synthesised in 1964 1,2,3,4,5-pentadeuterocyclopentadiene and established that, when it is heated to 45–65 °C, the hydrogen atoms are distributed uniformly among the 1-, 2-, and 5-positions of the cyclopentadiene ring and the reaction is not accompanied by hydrogen exchange. This confirmed the conclusions of Mironov et al.[20,26] Roth[28] obtained the kinetic parameters of the isomerisation of pentadeuterocyclopenadiene: $\Delta G^{\neq} = 24.3$ kcal mol^{-1}# and $\lg A = 12.06$.

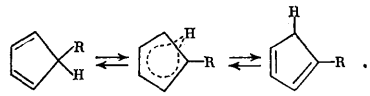
The experiments of Mironov and coworkers[22,23,26] on the synthesis and isomeric transformations of diene (IV) were reproduced[29–31], the first order of the reaction was confirmed, and $\Delta H^{\neq} = 20.4$ kcal mol^{-1} and $\Delta S^{\neq} = -10$ e.u. were found for the transformation (IV) → (V). It has been established[29] that the rate of reaction does not change when the sample of the given substance is diluted with carbon tetrachloride or when the reaction is carried out in a platinum vessel. The data of Mironov and coworkers[16,22,25,26] concerning the composition of the equilibrium mixtures of mono- and di-methylcyclopentadienes were also confirmed[29,30]. The same workers[31] reproduced the earlier experiments[20,26] on the synthesis of isomerisation of 5-deuterocyclopentadiene.

Using a method similar to that described by Mironov and coworkers[22,23,26], McLean et al.[32] synthesised in 1969 2-methylpentadeuterocyclopentadiene, compared the kinetic parameters of its conversion into the 1-isomer ($\Delta H^{\neq} = 22.35$ kcal mol^{-1}, $\Delta S^{\neq} = -6.2$ e.u.) with the corresponding values for 2-methylcyclopentadiene ($\Delta H^{\neq} = 19.9$ kcal mol^{-1}, $\Delta S^{\neq} = -10.8$ e.u.), and calculated the isotope effect $k_H/k_D = 6$. The measured quantity represents the sum of the primary kinetic isotope effect and the secondary effect generated by the four D atoms attached to the double bonds, but the latter hardly constitutes 10% of the value quoted. Thus the

† The non-traditional designation of electron transfer in this review (and in the papers quoted) is used in order to emphasise that the essential feature of the 1,5-shift is the migration of precisely the system of two double bonds.

Here and henceforth, the conversion of the values of $\Delta G^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ quoted in this review to the SI system requires their multiplication by 4.18.

primary kinetic isotope effect of the 1,5-hydrogen shift in the series of cyclopentadienes greatly exceeds the value which might have been expected from the difference between the dissociation energies of the C–D and C–H bonds. This shows that in the transition state the migrating hydrogen (deuterium) atom is equidistant from the initial ($C_{(5)}$) and final ($C_{(1)}$) migration centres:



This mechanism has also been confirmed by the high negative entropy of activation for the reaction $\Delta S^{\neq} = -8$–10 e.u., corresponding to a rigorously ordered transition state, which also explains satisfactorily the rigorous sequence of the interconversions of the isomers.

Virtunlly all subsequent studies[33–50] on cyclopentadiene derivatives were carried out taking into account the high rate of their isomerisation. The rate of the isomeric transformations of cyclopentadienes depends significantly on the nature of the substitution. Thus in 5-substituted cyclopentadienes the 1,5-shift of hydrogen takes place at a rate much higher than in their isomers with a free methylene group[22,23]. The accumulation of alkyl groups in the cyclopentadiene ring lowers the rate of reaction appreciably[26,30]. Electron-accepting substituents apparently exert the opposite effect[5].

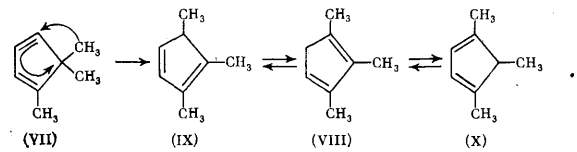
The kinetic measurements described above were performed for the virtually irreversible reaction (IV) → (V). Recently a study has been made[51] of the kinetics of the reversible isomerisation of thermodynamically stable cyclopentadienes, namely (V) ⇌ (VI), starting with the pure diene, at 50–80 °C. The values obtained were $\Delta H^{\neq} = 20.5$ kcal mol^{-1} and $\Delta S^{\neq} = -15.7$ e.u. for the reaction (VI) → (V) and $\Delta H^{\neq} = 20.6$ kcal mol^{-1} and $\Delta S^{\neq} = -15.1$ e.u. for the reaction (V) → (VI). It is striking that, within the limits of the accuracy of the measurements, the enthalpies of activation for the reactions (IV) → (V) [29,32] and (V) → (VI) [51] are the same. This permitted the conclusion[51] that the sharp difference between the rates of the above processes is virtually caused solely by the entropy factor. In other words, the difference between the rates of the 1,5-shift of hydrogen in cyclopentadienes which are isomeric as regards the position of the system of endocyclic double bonds is determined mainly by the entropy of activation. Hence the relative thermodynamic stability of isomers and correspondingly their concentrations in the equilibrium mixture should depend to a large extent on their entropies.

The compositions of the equilibrium mixtures of substituted cyclopentadienes have now been fairly thoroughly investigated and the general trend is known—5-substituted cyclopentadienes are energetically less favourable than their isomers with a free methylene group[26]. The change in the nature of the alkyl group in monoalkylcyclopentadienes is not reflected in the composition of the equilibrium mixture (1- and 2-alkylcyclopentadienes in proportions of 44 : 56).[52] As a result of the presence in the cyclopentadiene ring of substituents lengthening the conjugation chain, the dominant isomer (not lets than 95%) in the mixture has the structure of the 1-isomer (phenylcyclopentadiene[9], cyclopentadienecarboxylic acid[3,7,53], its methyl ester[3,7], and chloride[54]). However, the introduction of the same groups in the side chain of an alkylcyclopentadiene, even in the α-position, hardly affects the composition of the equilibrium mixture compared with alkylcyclopentadienes[55].

It is known[31,56] that the migration of the system of double bonds in cyclopentadienes is accelerated by strong bases. Thus, in the presence of sodium amide in liquid ammonia, the alkylation of the cyclopentadienyl anion leads directly to equilibrium mixtures of alkylcylopentadienes even at 240 K.[52,56,57] Sodium hydroxide in methanol also catalyses the isomeric transformations of cyclopentadienes[31]. However, under the conditions of alkaline catalysis hydrogen exchange takes place in cyclopentadienes[31]; presumably in this instance the reaction proceeds via a mechanism different from that indicated above, namely via the heterolytic dissociation of the C–H bond in the 5-position in the cyclopentadiene ring with subsequent protonation of the resulting cyclopentadienyl anion.

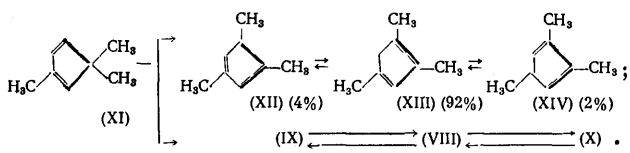
2. The 1,5-Shift of the Alkyl Group

The irreversible thermal isomerisation of 1,5,5-trimethylcyclopentadiene (VII) to 1,2,3-trimethylcyclopentadiene (VIII) in the gas phase at 623 K has been observed[4]. It was subsequently established[56,58–61] that this reaction leads to an equilibrium mixture of vicinally substituted trimethylcyclopentadienes, in which isomer (VIII) predominates[24]:



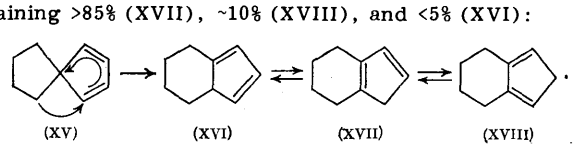
The following kinetic parameters have been obtained for this reaction: $\Delta H^{\neq} = 40.3$ kcal mol^{-1} and $\Delta S^{\neq} = -1$ e.u. (350° to 400 °C) according to the data of de Haan and Kloosterzieb[58,59] and $\Delta H^{\neq} = 43.8$ kcal mol^{-1} and $\Delta S^{\neq} = 0.7$ e.u. (328–430 °C) according to the data of Herndon and Manion[60,61].

Isomerisation of the same type has been observed[59] in relation to 2,5,5-trimethylcyclopentadiene [$\Delta H^{\neq} = 44.2$ kcal mol^{-1} and $\Delta S^{\neq} = 6$ e.u. for the reaction (XI) → (VIII) + (IX) + (X) and $\Delta H^{\neq} = 44.4$ kcal mol^{-1} and $\Delta S^{\neq} = 3$ e.u. for the reaction (XI) → (XII) + (XIII) + (XIV)]:



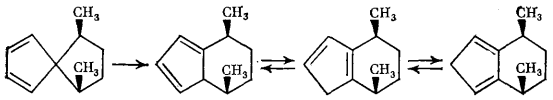
Like compound (XI), 5,5-dimethylcyclopentadiene[56,62] is converted at 220–330 °C into a mixture of 1,2- and 2,3-dimethylcyclopentadienes ($\Delta H^{\neq} = 43.3$ kcal mol^{-1} and $\Delta S^{\neq} = 3$ e.u.[62]).

Isomerisation involving spiran cyclopentadienes can proceed via the same mechanism; thus spiro[4,4]nona-2,4-diene (XV) is smoothly converted at 503–593 K in the gas phase[63,64] into an equilibrium mixture of compounds of the tetrahydroindene series—bicyclo[4,3,0]nonadienes (XVI), (XVII), and (XVIII), containing >85% (XVII), ~10% (XVIII), and <5% (XVI):



The results of Mironov and coworkers[63,64] were subsequently confirmed[65]; the following kinetic parameters were obtained for the reaction (XV) → (XVI) + (XVII) + (XVIII): $\Delta H^{\neq} = 34.6$ kcal mol^{-1} and $\Delta S^{\neq} = -1$ e.u. The study of the same reaction in relation to the *cis*- and *trans*-6,9-dimethylspiro[4,4]nona-2,4-dienes showed[66] that the isomerisation

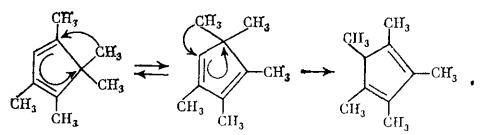
takes place rigorously stereospecifically with retention of the configuration of the initial compound, for example:



An analogous isomerisation has been observed for spiro-[4,5]deca-2,4-diene[65] ($\Delta H^{\neq} = 45.5$ kcal mol^{-1} and $\Delta S^{\neq} = 6$ e.u.). The composition of the equilibrium mixture of bicyclo[5,3,0]decadienes formed [90% of the 1(5),2-isomer] is extremely close to that mentioned above for the analogue with a six-membered ring. It is of interest that the isomerisation of spiro[4,3]octa-2,4-diene to a mixture of bicyclo-[3,3,0]octadienes [the 1,4- and 1(5),2-isomers in proportions of 1 : 1.3], with conversion of the four-membered ring into a five-membered ring[67], takes place already at 100 °C, i.e. much more readily than for the analogues described above ($\Delta G^{\neq} = 29.2$ kcal mol^{-1}, $\lg A = 13.8$)§. This reaction is virtually irreversible, because the isomers of cyclopentadienes containing two alkyl groups in the 5-position are thermodynamically unstable (cf. the 5-substituted cyclopentadienes described above).

In all the cases mentioned above the isomerisation of 5,5-disubstituted cyclopentadienes takes place selectively via the intramolecular migration of the alkyl group from the 5-position to a neighbouring carbon atom (via the 1,5-shift mechanism), since the reaction results in the elimination of the geminal substitution and the formation of 1,3-shift products has not been observed in any instance. In the concluding stage of the process equilibrium is established between isomers which differ by the positions of the endocyclic double bonds as a result of the 1,5-shift of hydrogen at a higher rate than the shift of the substituent.

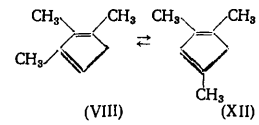
The thermal transformations of a series of 5,5-disubstituted cyclopentadienes, in which the 1,5-shift of the alkyl group should not lead to the elimination of geminal substitution, i.e. to cyclopentadienes with substituted 1- and 4-positions, have been investigated. It has been established[69–71] that 1,2,4,5,5-pentamethylcyclopentadiene (XIX) is converted at 400–500 °C (contact time ~8 s) into 1,2,3,4,5-pentamethylcyclopentadiene (XX) with 1,2,3,4,5-pentamethylcyclopentadiene (XXI) as the intermediate:



(XIX) (XXI) (XX)

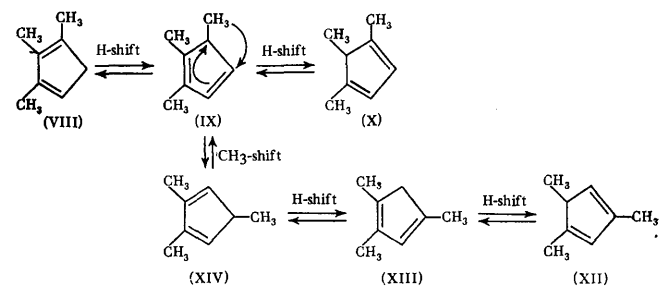
The formation of a *gem*-substituted diene (XXI) at intermediate stages shows that the reaction is a combination of two consecutive 1,5-shifts of the methyl group. The first, rate-limiting stage is the reversible isomerisation (XIX) ⇌ (XXI), which does not affect the geminal substitution; the second, irreversible stage (XXI) → (XX) leads to a thermodynamically stable diene, in which there is a possibility of a 1,5-shift of hydrogen. An analogous transformation at a somewhat lower temperature (330–460 °C) has been observed for 1,4,5,5-tetramethylcyclopentadiene[56,72].

In thermodynamically stable cyclopentadienes (with a free methylene group) reversible skeletal isomerisation, which leads to equilibrium mixtures of dienes differing in the nature of substitution, is observed at 400–500 °C (contact time ~8 s). An isomerisation of this type was observed for the first time in 1968 by Mironov and coworkers[73–75], who showed that at 400–500 °C 1,2,3- and 1,2,4-trimethylcyclopentadienes (VIII) and (XIII)¶ form an equilibrium mixture containing 55% of the "1,2,3-isomers" (VIII)–(X) and 45% of the "1,2,4-isomers" (XII)–(XIV):



(VIII) (XII)

The recorded rate of isomerisation (VIII) → (XII) is appreciably higher than that of the reverse reaction (XII) → (VIII), while the ratio of the concentrations of the groups of isomers [(VIII)–(X)] : [(XII)–(XIV)] in the state of equilibrium is 1.22 : 1. Hence it was concluded[73–75] that structures (VIII) and (XII) are not directly responsible for the transformation under discussion and that the intermediates are 5-substituted cyclopentadienes. Bearing in mind that the rate of reaction is satisfactorily correlated with the content of isomers (IX) and (XIV) in the corresponding initial equilibrium mixtures, the following scheme was considered as the reaction mechanism:



The initial stage of the process is migration of hydrogen leading to an unstable isomer containing the migrating substituent in the 5-position. The rate-limiting stage of the isomerisation is the reversible intramolecular 1,5-shift of the methyl group (IX) ⇌ (XIV). In the concluding stage of the reaction equilibrium with respect to the positions of the double bonds is established for an isomer with another type of substitution.

Under similar conditions, reversible skeletal isomerisation of 1,2- and 1,3-dimethyl-substituted[76] and also of 1,2- and 1,3-di-s-butyl-substituted cyclopentadienes[57] has been observed. In both cases equilibrium mixtures of isomers, differing in the relative positions of the substituents, were obtained. It was noted[57] that the rate of migration of the s-butyl group is higher than that of the methyl group.

1,2,3,4-Tetramethylcyclopentadiene, containing a [^{14}C]-labelled methyl group in the 1(4)-position, has been synthesised and its thermal transformations have been investigated[77]. It has been established that at 400–500 °C the label is uniformly distributed between the methyl groups in the 1(4)- and 2(3)-positions; the appearance of a labelled carbon atom in the ring was not noted. This result agrees well with the mechanism of the isomerisation of thermodynamically stable cyclopentadienes described above, in which the main stage is the reversible thermal intramolecular 1,5-shift of the alkyl group and it makes it possible to rule out unambiguously the

§ The thermal transformations of spiro[4,2]hepta-2,4-diene takes place in a different way, leading to a complex mixture of hydrocarbons containing 6-methylfulvene, allylcyclopentadienes, and 1,2-dimethylcyclopent-3-ene[63,68].

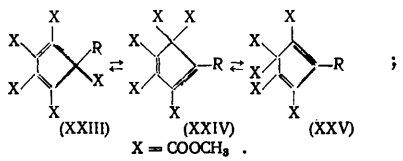
¶ More precisely the corresponding equilibrium mixtures of isomers with respect to positions of the double bonds in which the given dienes predominate.

alternative mechanism involving the rupture of the cyclopentadiene ring at the $C_{(1)}$–$C_{(5)}$ bond and subsequent recyclisation in the direction of CH_3 at $C_{(1)}$–$C_{(4)}$ (with transfer of the reaction centre and the shift of a hydrogen atom—cf. Section IV).

Thus in the series of substituted cyclopentadienes four types of migration of the alkyl group at 200–450 °C, leading to a change in the nature of the substitution, have been observed: (1) reversible thermal isomerisation of 5,5-disubstituted cyclopentadienes, which does not affect the geminal substitution; (2) irreversible thermal isomerisation of 5,5-disubstituted cyclopentadienes to dienes with a free methylene group; (3) irreversible thermal isomerisation of 5,5-disubstituted cyclopentadienes containing substituents in the 1- and 4-positions to dienes with a free methylene group, which constitutes a combination of the two types of isomerisation specified above; (4) reversible thermal isomerisation of cyclopentadienes with a free methylene group, which leads to the formation of equilibrium mixtures of dienes differing in the nature of the substitution.

The 1,5-shift of the alkyl group is independent of the type of substitution and constitutes a general feature of the series of cyclopentadienes. One must note that in each case the 1,5-shift of the alkyl substitutent is accompanied by the migration of the system of endocyclic double bonds, which indicates the similarity of the phenomena under discussion to the 1,5-shift of hydrogen. The transition state in reactions involving the 1,5-shift of an alkyl group is apparently also close to that described for the hydrogen shift. This is confirmed by the rigorously consecutive sequence of transformations and their stereospecificity.

The substitutents in the cyclopentadiene ring other than alkyl groups are also capable of migrating. Thus it has been observed[78–80] that the group $COOCH_3$ can migrate via the 1,5-shift mechanism, for example, in compounds (XXIII)–(XXV):



(XXIII) (XXIV) (XXV)

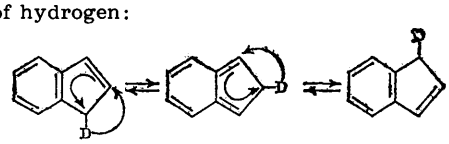
X = $COOCH_3$.

At 100–150 °C the transformation (XXIII) → (XXIV) takes place and at higher temperatures transformation (XXIV) → (XXV) occurs. The results of kinetic measurements for isomerisation of the type (XXIII) → (XXIV) are presented in Table 1. The reaction is of first order and the entropy of activation is typical for a 1,5-shift. It is striking that the migration of the methoxycarbonyl group takes place much more readily than that of an alkyl group but with much more difficulty than the 1,5-shift of hydrogen. It is noteworthy that the rate of isomerisation (XXIII) → (XXIV) depends significantly on the nature of the ring substituent (Table 1).

On the basis of the data of Bladon et al.[81], it can be postulated that the phenyl group in cyclopentadienes migrates under less severe conditions than the methyl group: according to Bladon et al.[81], the reduction–dehydration of 3,4-diphenylcyclopent-3-en-1-one (with distillation of the reaction product at 250 °C) leads to the formation of 1,4-diphenylcyclopentadiene and not the 1,2-isomer, the former being evidently the product of the skeletal isomerisation of the 1,2-isomer formed initially via the mechanism described above. Thus in the cyclopentadiene series there is a possibility of both the 1,5-shift of hydrogen (20–80 °C) and the 1,5-shift of substituents (100–400 °C). The latter takes place under much more severe conditions and is accompanied by the 1,5-shift of hydrogen in the final and sometimes also the initial dienes.

III. INDENES

It was shown in 1964 [28] that heating of 1-deuteroindene (XXVI) at 200 °C leads to a uniform distribution of deuterium between the three non-aromatic carbon atoms in the absence of hydrogen exchange between the molecules. Hence, by analogy with cyclopentadienes[26], it was concluded[28] that in compounds of the indene series there is a possibility of a 1,5-shift of hydrogen:



(XXVI) (XXVII) (XXVIII)

Despite the fact that the reaction proceeds in the given instance via a stage involving the formation of the energetically unfavourable isoindene (XXVII), it always involves a 1,5-shift and not a 1,3-shift, in which the above stage is missing.

Table 1. Kinetic parameters of the 1,5-shift of the $COOCH_3$ group in 5-R-pentamethoxycarbonylcyclopentadienes (XXIII) → (XXIV)*.

R	t, °C	Solvent	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, e.u.	Refs.
$N(CH_3)_2$	49–80	DCB**	21.7	−12.1	[80]
NHC_6H_5	49–80	DCB	21.2	−11.6	[80]
CN	85–129	DCB	24.0	−10.3	[80]
OCH_3	96–129	DCB	22.4	−15.0	[80]
C_6H_5	93–128	DCB	25.5	−10.6	[80]
CH_3COOCH_3	113–150	chlorobenzene	25.3	−9.7	[78]
	99–129	DCB	27.8	−4.8	[79]
$CH_3COOC_2H_5$	97–120	toluene	25.3	−10.9	[78]
	97–120	chloroform	25.2	−10.9	[79]
CH_3	104–144	DCB	26.9	−8.6	[79]
C_2H_5	99–129	DCB	29.3	−3.4	[79]
$CH(CH_3)_2$	99–129	DCB	30.6	+1.2	[79]
SCH_3	119–155	DCB	25.0	−13.4	[80]
Cl	150–190	DCB	27.3	−10.3	[79]

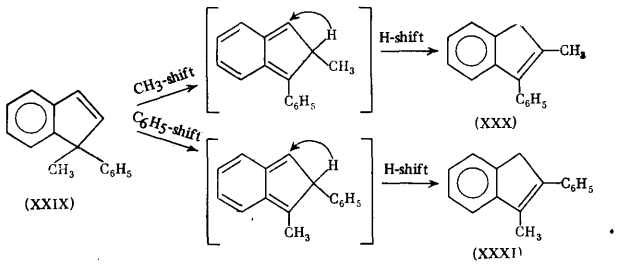
* The compounds are listed in order of decreasing rate of reaction.

**DCB = *o*-dichlorobenzene.

The isomerisation of indenes is known to be catalysed by bases, including amines[82,83]. However, a feature of such catalytic reactions, which has not so far been explained, is their stereoselectivity[84,85] and the virtual absence of hydrogen exchange[85].

The migration of a substituent in the indene series has been known for a relatively long time. In an early study Ziegler and Crössman (1929) observed[86] the irreversible isomerisation of 1,3,3-triphenylindene to 1,2,3-triphenylindene at 400 °C (the reaction mechanism was not discussed). At 450 °C thermodynamic equilibrium is established between the isomeric 1,3-, 1,2-, and 2,3-diphenylindenes[87]. Under the same conditions, the isomerisation of 1-methyl-1,3-diphenylindene to a mixture of 1-methyl-2,3-diphenyl- and 3-methyl-1,2-diphenyl-indenes has been observed[87]. The experimental data described can now be readily interpreted by a combination of consecutive 1,5-shifts of the substituent and hydrogen, by analogy with that described in the preceding Section. The 1,5-shift of substituents in indenes has

been observed directly in a study[88] devoted to the thermal transformations of 1-methyl-1-phenylindene (XXIX):

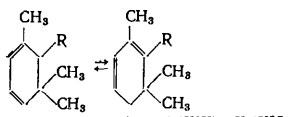


The ratio of isomers (XXX) and (XXXI) shows that the ability to migrate decreases in the sequence H ≫ C_6H_5 > CH_3, i.e. in the sequence mentioned above for cyclopentadienes. It has been reported[88] that the transformations (XXIX) → (XXX) and (XXIX) → (XXXI) are first-order reactions. Thus one must assume that the 1,5-shift reaction in the indene series has virtually the same features as for the cyclopentadienes.

IV. CYCLOHEXA-1,3-DIENES

1. The 1,5-Shift of Hydrogen

The interconversions of cyclohexa-1,3-dienes isomeric with respect to the position of the system of endocyclic double bonds were first observed in 1950 [89] in relation to the reversible isomerisation of 1,5,5,6- and 1,2,6,6-tetramethylcyclohexa-1,3-dienes (XXXII) and (XXXIII) at 350 °C, but the reaction mechanism was not investigated†:



(XXXII), (XXXIV) (XXXIII), (XXXV)

(XXXII), (XXXIII): R = CH_3

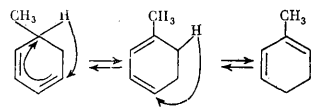
(XXXIV), (XXXV): R = H

The reversible isomerisation of 1,5,5- and 2,6,6-trimethylcyclohexa-1,3-dienes (XXXIV) and (XXV) at 300–400 °C was described[90] in 1956. It was suggested that the reaction proceeds via a "biallyl biradical" mechanism, which, in terms of modern terminology, involves ring rupture (with formation of a substituted hexatriene), the 1,7-shift of hydrogen in the resulting triene, and subsequent recyclisation (see below)#. In relation to the type of isomerisation considered, this mechanism aroused serious doubts, because it implied a change in the type of substitution during the reaction and the possibility of the degeneracy of the rearrangement to "automerisation" or a transformation without a change in the structure of the substance, for example, in the case of 5-methylcyclohexa-1,3-diene or 1,5,5-trimethylcyclohexa-1,3-diene (the isomerisation of the latter was observed in the same study[90]).

By analogy with the known behaviour of cyclopentadienes, it was later suggested[95] that the above reaction proceeds via the 1,5-shift of hydrogen and is completed by the attainment of thermodynamic equilibrium [(XXXIV) : (XXXV) ≅ 1 : 1]. An analogous hypothesis had been put forward in an earlier study[93].

In 1971 the migration of the system of double bonds in the cyclohexa-1,3-diene ring was investigated by the authors of this review[96,97]. All three possible isomeric methylcyclohexadienes with a high degree of purity were synthesised and their thermal transformations were investigated[96–98]. It was established[96,97] that the reversible isomerisation of 1-, 2-, and 5-methylcyclohexadienes (XXXVI), (XXXIII), and (XXXVIII) takes place at 300–420 °C and that each diene gives rise to the same equilibrium mixture: 57% (XXXVI), 30% (XXXVII), and 13% (XXXVIII)§.

A study of the compositions of mixtures of methylcyclohexa-1,3-dienes at various equilibration stages starting from the individual dienes (XXXVI)–(XXXVIII) showed[96] that the isomers are interconverted consecutively:



(XXXVIII) (XXXVI) (XXXVII)

The above sequence of transformations is typical for the 1,5-shift of hydrogen, which enabled the authors[96,97] to consider precisely this reaction mechanism. The following kinetic parameters of the isomerisation (XXXVIII) ⇌ (XXXVI) have been obtained[98] for the temperature range 230–250 °C: $\Delta H_1^{\neq} = 38.8$ kcal mol^{-1} and $\Delta S_1^{\neq} = -11.2$ e.u. for the reaction (XXXVIII) → (XXXVI) and $\Delta H_2^{\neq} = 38.5$ kcal mol^{-1} and $\Delta S_2^{\neq} = -14.5$ e.u. for the reaction (XXXVI) → (XXXVIII). In another study[106], where the isomerisation (XXXVIII) → (XXXVII) was regarded as an irreversible reaction, $\Delta G^{\neq} = 35.2$ kcal mol^{-1} and $\lg A = 11.2$ were obtained for the temperature range 300–360 °C. The high negative entropies of activation permitted the conclusion[98] that the reaction has a sigmatropic mechanism with a rigorously ordered transition state and the "biallyl biradical" mechanism could be ruled out[90,107], since if the latter operated the first and rate-limiting stage should have been ring opening with formation of acyclic trienes, to which positive values of $\Delta S^{\neq}$ would have corresponded.

It is striking that for significantly different rates of the reactions (XXXVIII) → (XXXVI) and (XXXVI) → (XXXVIII) (for example, the corresponding rate constants at 230 °C are 5.3×10^{-5} s^{-1} and 2×10^{-5} s^{-1}) the enthalpies of activation for the reactions are the same to within a high degree of accuracy. It has therefore been suggested[98] that the difference between the rates of the interconversions of cyclic dienes isomeric with respect to the position of the system of double bonds is determined almost entirely by the entropy factor.

Simultaneously with the above investigations[96,97] and independently of them, it has been shown[108] that mixtures of isomeric methylcyclohexa-1,3-dienes undergo a change in composition at 300–350 °C, i.e. the dienes isomerise under the experimental conditions. It has been suggested[108] that such isomerisation involves the 1,5-shift of hydrogen but no

† The formation in the synthesis of cyclohexa-1,3-dienes of isomers whose structures differ from that expected on the basis of the reaction mechanism has been observed[91–94].

The isomerisation of acyclic 3-*cis*-1,3,5-trienes to cyclohexa-1,3-dienes is one of the most thoroughly investigated electrocyclic reactions[99–104]; the process takes place quantitatively at 100–200 °C. The possibility of the reverse reaction under the conditions of the pyrolysis has been confirmed indirectly by data[105] for the conversion of cyclohexa-1,3-diene into 3-*trans*-hexa-1,3,5-triene (530 °C, yield 1%).

§ Under the given conditions, the isomerisation is not accompanied by the formation of appreciable amounts of side products; among side reactions, the aromatisation of methylcyclohexadienes via their thermal dehydrogenation[96] becomes appreciable only at 450 °C and above.

arguments in support of this have been adduced. It has also been suggested[108] that the process should lead to the establishment of thermodynamic equilibrium between the isomers, but this was not attained.

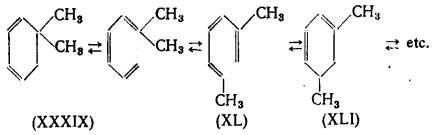
In subsequent studies[109–111] the 1,5-shift was widely used to account for the isomeric transformations of cyclohexa-1,3-dienes.

The information about the composition of the equilibrium mixtures of substituted cyclohexa-1,3-dienes is at present extremely limited, but the data available on this problem[94–96, 111] show that it is close to that of the equilibrium mixtures in the series of cyclopentadienes, which has been much more thoroughly investigated.

It is known that the isomeric transformations of cyclohexadienes can be catalysed by both acids[112] and bases[113], but in both cases the reaction mechanism is evidently different from the 1,5-shift of hydrogen.

2. The 1,5-Shift of the Substituent

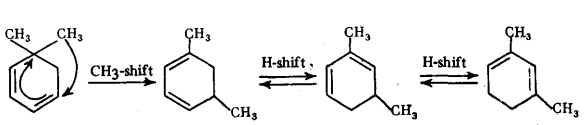
The migration of an alkyl group in the series of cyclohexa-1,3-dienes was first observed in 1956.[90,107] It was established[90] that 5,5-dimethylcyclohexa-1,3-diene (XXXIX) isomerises at 500 °C to 1,3-disubstituted cyclohexadienes, the process being accompanied by aromatisation (to the extent of ~25%; the aromatic fraction contained 33% of toluene and 67% of *m*-xylene). Analogous transformations are undergone by 1,5,5- and 2,6,6-trimethylcyclohexa-1,3-dienes (XXXIV) and (XXXV), forming 1,3,5-trimethyl-substituted cyclohexadienes, mesitylene, and *m*-xylene. The biallyl biradical mechanism has been proposed for the above skeletal isomerisation[90,107]:



(XXXIX) (XL) (XLI)

A characteristic feature of the process involving this mechanism should be a change in the type of substitution and the incorporation of the carbon atom of the side chain in the ring. It was believed that the ability of 5-ethylcyclohexa-1,3-diene (XLII) also to undergo skeletal isomerisation at 450–500 °C, leading to mixtures of 1,2- and 1,4-dimethyl-cyclohexa-1,3-dienes and the corresponding aromatic compounds, constitutes confirmation of this mechanism. It is noteworthy that the degree of conversion of the diene (XLII) into its skeletal isomer is extremely low (not more than 30% at 500 °C, including xylenes).

In 1971 the authors of this review[114,115] carried out an experimental test of the mechanism of the skeletal isomerisation of 5,5-disubstituted cyclohexadienes and established that at 430–530 °C 1,5- and 1,3-dimethylcyclohexa-1,3-dienes (XLI) and (XLII) are formed from the diene (XXXIX) as a result of the consecutive transformations (XXXIX) → (XLI) → (XLIII), corresponding to a mechanism involving the 1,5-shift of the methyl group:



(XXXIX) (XLI) (XLII) (XLIII)

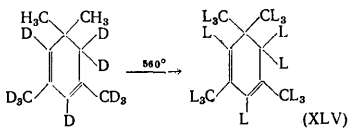
In the concluding stage of the reaction the diene (XLI) formed initially is converted as a result of the 1,5-shift of hydrogen (see above) into an equilibrium mixture of isomers, in which the diene (XLIII) predominates. The reaction is accompanied by aromatisation, toluene being formed from the initial diene (XXXIX) as a result of thermal demethylation and *m*-xylene being formed from the isomerisation products.

It has been noted[114] that the potential barrier to skeletal isomerisation in the series of cyclohexa-1,3-dienes exceeds only slightly the barrier to the hydrogen shift (in contrast to cyclopentadienes). Bearing in mind that, under the conditions of the hydrogen shift, ring opening is known not to occur (see above), presumably the skeletal isomerisation occurring under virtually the same conditions does not involve a ring opening–recyclisation mechanism[90,107] but proceeds via the 1,5-shift of the substituent.

In 1972 Spangler and Bolos[116] arrived independently at the same conclusions. As an additional argument against the ring rupture–recyclisation mechanism, they quoted the observation that the reaction products do not contain any acyclic derivatives of hexatriene. Furthermore, a special synthesis of the triene (XL) (in a mixture with the *trans,trans*-isomer), which might have been an intermediate in the ring dissociation–recyclisation process, was carried out and it was observed that during pyrolysis under identical conditions the diene (XXXIX) and the triene (XL) give rise to completely different mixtures of products[116].

Thus it was established that the irreversible 1,5-shift of the alkyl substituent takes place in 5,5-disubstituted cyclohexa-1,3-dienes in the temperature range 400–500 °C and leads to the elimination of geminal substitution, being completed by the 1,5-shift of hydrogen.

It has been observed[117] that the pyrolysis products of 1,3,5,5-tetramethylcyclohexa-1,3-diene (XLIV) with deuterium atoms in all the positions except for the two geminal methyl groups contain at 560 °C only 19% of the diene (XLV) (the rest consists of mesitylene and methylbenzenes). According to mass spectrometric data, in the absence of hydrogen exchange between the molecules the label is redistributed among the possible positions:



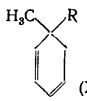
(XLIV) $L = {}^3/_8H + {}^5/_8D$. (XLV)

The above phenomenon was regarded[117] as proof of the ring dissociation–recyclisation mechanism for thermal transformations of the diene (XLIV). However, it is striking that the migration of the alkyl group in the cyclohexa-1,3-diene series takes place at an incomparably higher temperature than in the given experiment. We may note that the results of the above study[117] confirm unambiguously an intramolecular mechanism of the isomerisation of cyclohexadienes even under the very severe conditions used.

According to Schiess and Dinkel[118], the rate of the thermal isomerisation of 5,5-diethylcyclohexa-1,3-diene is 8 times higher than for the dimethyl analogue. At 500 °C (1 s) the reaction is accompanied by a change in the type of substituent; as a result of this (as well as aromatisation), the mixture obtained contains not less than 30 components. The change in the type of substituent can be associated in this instance solely with the rupture of the ring and recyclisation. However, the problem of the nature of the given skeletal isomerisation at 300–400 °C, i.e. under what conditions it should occur if the comparative data of Schiess and Dinkel[118] concerning its rate are correct [cf. the above considerations for the diene (XXXIX)], remains open.

At 300–500 °C non-alkyl groups, for example, the formyl, acetyl, and methoxycarbonyl groups, are capable of migrating in the ring of cyclohexa-1,3-diene.[119] The reaction

results in a mixture of products corresponding to a mechanism involving the 1,5-shift of the substituent with a subsequent 1,5-shift of hydrogen and is accompanied by extensive aromatisation (particularly on prolonged heating). Kinetic measurements[106], the results of which are presented in Table 2, permitted the conclusion that the formyl group in the cyclohexadiene ring migrates at a higher rate than hydrogen, while the methoxycarbonyl and acetyl groups migrate at a lower rate (the rate of migration of the methyl groups is lower still). The pre-exponential factors obtained[106] correspond to a high negative entropy of activation for the reaction, characteristic of the 1,5-shift.



(XLVI)

R = $COOCH_3$(a), $COCH_3$(b), CHO (c), or C_6H_5 (d).

Table 2. Kinetic parameters of the thermal isomerisation of 5,5-disubstituted cyclohexa-1,3-dienes[106].

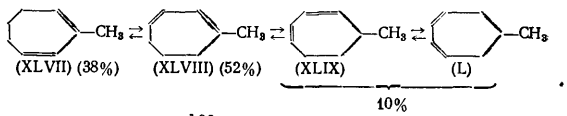
Compound	R	t, °C	$\Delta G^{\neq}$, kcal mol^{-1}	lg$A$
(XLVIa)	$COOCH_3$	270—304	40.8	11.8
(CLVIb)	$COCH_3$	200—240	35.9	12.1
(XLVIc)	CHO	150—200	31.0	11.5

The pyrolysis of 5-methyl-5-methoxycarbonyl- and 5-methyl-5-phenyl-cyclohexa-1,3-dienes (XLVI, a and d), containing a ^{13}C atom in the methyl group in the 5-position, has been investigated[118]. It was established[118] that the label in the methyl group of the diene (XLVIa) is retained to the extent of 85% at 300 °C (1 h in heptane) and 75% at 520 °C (1 s). On the other hand, in the pyrolysis products of compound (XLVId) at 550 °C (1 s) 96% of the label is concentrated in the main ring (disregarding the substituents) and only 4% in the methyl group. On the basis of foregoing, the authors[118] concluded that the migration of the substituents via the 1,5-shift mechanism takes place only when its rate is as high as for a hydrogen atom or a carbonyl group; otherwise the ring dissociation—recyclisation mechanism operates preferentially. However, the experimental data quoted by the authors[118] for the diene (XLVId) involve an evident error: in the statistical distribution of the label in the cyclohexadiene ring and in the methyl group as a result of repeated ring dissociation—recyclisation steps the content of the label in the methyl group cannot be less than ~14% (for a system comprising seven carbon atoms). Bearing in mind the above experimental error, one must suppose that above 500 °C some of the labelled carbon atoms of the methyl group enter the cyclohexadiene ring in the isomerisation process [at 530 °C this fraction is much smaller for the diene (XLVIa) than would be expected for a statistical distribution]. This agrees satisfactorily with the data described above[117].

Thus in 5,5-disubstituted cyclohexa-1,3-dienes different substituents, including alkyl substituents and those containing the carbonyl group, particularly the formyl substituent, should migrate via the 1,5-shift mechanism. Above 500 °C the reaction involves ring dissociation—recyclisation (with a 1,7-shift of hydrogen in the intermediate acyclic triene structure). It is reasonable to regard the latter process as a side reaction and not a parallel reaction, since the 1,5-shift of the substituent takes place already at 400 °C. The concluding stage of the process is in this instance the 1,5-shift of hydrogen in the resulting structures which do not contain geminal substituents.

V. CYCLOHEPTA-1,3-DIENES

In 1970 Mironov and coworkers[120–123] described the synthesis and isomeric transformations of methyl- and monodeuterocyclohepta-1,3-dienes and established that at 120–160 °C in the liquid or gas phase 2-methylcyclohepta-1,3-diene (XLVII) undergoes reversible thermal isomerisation leading to the formation of an equilibrium mixture of the 1-, 2-, 5-, and 6-isomers (XLVIII), (XLVII), (XLIX), and (L). Here the initial product is the diene (XLVIII) and the reaction proceeds via a mechanism corresponding to the 1,5-shift of hydrogen:



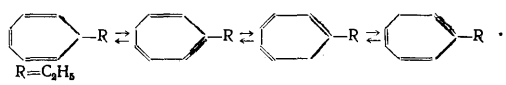
(XLVII) (38%) (XLVIII) (52%) (XLIX) (L)

10%

It has been established[122] that the reactions (XLVII) ⇌ (XLVIII) are of first order and have the following kinetic parameters: $\Delta H_1^{\neq} = 29.5$ kcal mol^{-1} and $\Delta S_2^{\neq} = -7.4$ e.u. for the reaction (XLVII) → (XLVIII) and $\Delta H_2^{\neq} = 28.6$ kcal mol^{-1} and $\Delta S_2^{\neq} = -9.9$ e.u. for the reaction (XLVIII) → (XLVII). Heating 2-deuterocyclohepta-1,3-diene at 140 °C leads[120,123] to a uniform distribution of deuterium between the possible positions in cycloheptadiene in the absence of hydrogen exchange between the molecules, which demonstrates an intramolecular reaction mechanism[123]. Thus it has been established unambiguously[120–123] that a reversible thermal intramolecular 1,5-shift of hydrogen takes place in the ring of cyclohepta-1,3-diene above 120 °C, leading to the establishment of thermodynamic equilibrium between the isomers with respect to the position of the system of endocyclic double bonds.

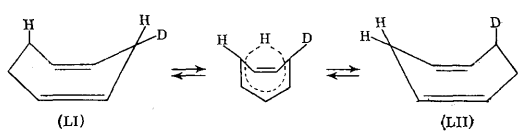
VI. CYCLOHEPTATRIENES

It has been established[124] that the pyrolysis of 7-ethylcycloheptatriene at 400 °C results in the formation of a mixture of all four possible isomers:



R=C_2H_5

A 1,5-shift of hydrogen, accompanied by the migration of the system of two double bonds, has been suggested. This mechanism has been convincingly confirmed[125,126] and it has been shown that, on heating 7-deuterocyclohepta-1,3,5-triene (LI) at 100–140 °C, the deuterium is distributed between the four possible positions. This transformation takes place via an intramolecular mechanism (there is no hydrogen exchange between molecules) and the initial isomerisation product of the triene (LI) is the 3-deutero-isomer (LII). It has been suggested[125] that a non-planar symmetrical structure is formed in the transition state:



(LI) (LII)

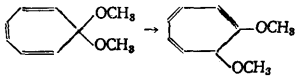
Subsequently the sequence of transformations of isomeric monosubstituted cycloheptatrienes (1,5-shift) was confirmed in a whole series of studies[127–137] dealing with the compositions of the equilibrium mixtures of cycloheptatrienes containing various substitutents [CH_3, C_6H_5, CN, OCH_3, SCH_3, $N(CH_3)_2$, p-$(CH_3)_2NC_6H_4$, COOH, or COOR]; a general tendency was demonstrated—the 7-isomers are energetically more favourable. It has been noted[129] that the presence of groups such as OCH_3 and particularly $N(CH_3)_2$ leads to a sharp increase of the rate of isomeric transformations. A thermal intramolecular 1,5-shift of hydrogen has also been observed in hexamethylcycloheptatrienes[138], in condensed systems containing the cycloheptatriene ring[139,140], in 1,4-di-(7-cycloheptatrienyl)benzene[141], and also in dihydrotropones[142].

The kinetic parameters of the thermal 1,5-shift of hydrogen in a series of cycloheptatrienes are presented in Table 3; a study was made of the transformation of the 7-isomer into the 3-isomer, which was regarded as irreversible. It has been noted[127,128] that the nature of the solvent does not affect the rate of isomerisation. In all the instances investigated the isomerisation was a first-order reaction. The extremely high negative entropy of activation for the reaction confirms the symmetry of the structure of the transition state. Thus it has been shown convincingly that a 1,5-shift of hydrogen takes place in cycloheptatrienes and involves only two of the three double bonds in the ring. The fairly close kinetic parameters of the isomerisation of methylcycloheptadienes and methylcycloheptatrienes constitute an additional confirmation of this fact.

Table 3. Kinetic parameters of the 1,5-shift of hydrogen in the series of cycloheptatrienes (7-isomer → 3-isomer).

Compound	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, e.u.	Refs.
7-Deuterocycloheptatriene	31	−10	[125]
7-Methylcycloheptatriene	33.3	−4.9	[136]
7-Phenylcycloheptatriene	27.6	−11.6	[127]
7-Methoxycycloheptatriene	25.7	−15	[137]
7-(4-Dimethylaminophenyl)-cycloheptatriene	27.6	−9.3	[130]
1,4-Di(7-cycloheptatrienyl)benzene	29.8	−3.9	[141]

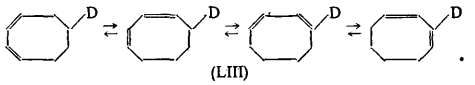
It has been established[143,144] that oxygen-containing substituents can migrate in cycloheptatrienes at 80–150 °C, for example:



This transformation has been observed[145] also in the ethylene ketal of cyclohepta-2,4,6-trien-1-one ($\Delta H^{\neq} = 23.2$ kcal mol^{-1} and $\Delta S^{\neq} = -23$ e.u.). The rate of migration of the methoxy-group in 7,7-disubstituted cycloheptatrienes exceeds, according to Hoffmann et al.[144], the rate of migration of hydrogen. The migration of the methoxy-group from the 7-position of the cycloheptatriene ring in trienes without geminal substituents has also been observed[144]. The combination of the shifts of a substitutent and hydrogen leads to the formation of extremely complex mixtures of compounds. According to some data[143–145], the migration of the alkoxy-group involves the 1,7-shift mechanism, i.e. all three double bonds of the cycloheptatriene ring participate in the transformation, which indicates a sharp difference between this reaction and the shift of substituents in related systems.

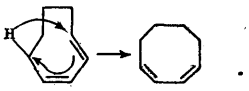
VII. CYCLO-OCTA-1,3-DIENES

In the study of the thermal transformations of 5-deutero-cyclo-octa-1,3-diene (LIII) in 1966 it was established[146] that the system of double bonds in the ring of cyclo-octa-1,3-diene migrates at 130–150 °C, which leads to the attainment of thermodynamic equilibrium between the isomers:



(LIII)

It has been shown[146] that the reaction is not accompanied by hydrogen exchange and that the sequence of the interconversions of the isomers corresponds to the scheme presented above. It has been noted that the reaction proceeds at comparable rates in the liquid and gas phases. The study of the kinetics of the isomerisation of the diene (LIII) in the temperature range 125–150 °C yielded $\Delta H^{\neq} = 29.3$ kcal mol^{-1} and $\Delta S^{\neq} = -10$ e.u. From the foregoing, it was concluded[146] that the reversible thermal intramolecular 1,5-shift of hydrogen takes place in cyclo-octa-1,3-dienes. In subsequent studies[147] of the quenching of the fluorescence of naphthalene under the influence of *cis,trans*-octa-1,3-diene (LIV) it was established that the observed phenomenon is due to the transformation of the diene (LIV) into its *cis,cis*-isomer (LV):

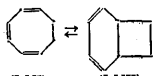


(LIV) (LV)

The authors[147] suggest that the isomerisation (LIV) → (LV) proceeds via the 1,5-shift of hydrogen ($\Delta G^{\neq} = 33$ kcal mol^{-1}).

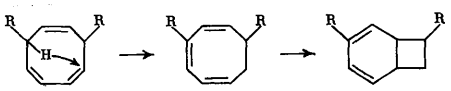
VIII. CYCLO-OCTATRIENES

The study of the migration of the system of double bonds in cyclo-octatrienes is complicated by the fact that the 1,3,5-isomer (LVI) readily undergoes the electrocyclisation reaction: as a result of the reversible reaction at 80–100 °C, equilibrium is established between the triene (LVI) (85%) and its valence tautomer—bicyclo[4,2,0]octa-2,4-diene (LVII) (15%):[148,149]



(LVI) (LVII)

The thermal isomerisation of 5,8-di(α-cyanoisopropyl)-cyclo-octa-1,3,6-triene (LVIII) to the corresponding bicyclic compound (LIX) in boiling xylene (20 h) or benzene (75 h) has been observed[150]:



(LVIII) (LX) (LIX)

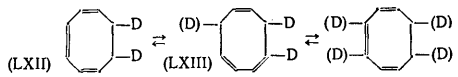
R = —C(CH$_3$)$_2$(C≡N)

The thermal isomerisation of the initial 1,3,6-triene (LVIII) to the 1,3,5-triene (LX) was regarded[150] as the intermediate stage of the reaction¶. By analogy with the isomerisation of

¶ The isolation of the homogeneous diene (LIX) from the reaction products is evidently associated with the loss of the isomer (LX) in the crystallisation process.

cycloheptatrienes described above, it was assumed that the reaction proceeds via the 1,5-hydrogen shift mechanism. The examination of a model of the initial compound led the authors[150] to the conclusion that the distance between the migrating H atom (at $C_{(5)}$) and the corresponding $C_{(1)}=C_{(2)}$ double bond is only 1.5 Å.

The reversible thermal isomerisation of cyclo-octa-1,3,6-triene (LXI) and cyclo-octa-1,3,5-triene (LVI) at 100–130 °C, leading to the formation of their equilibrium mixture containing slight (0.5–1%), but susceptible to determination amounts of the triene, (LXI), was described almost simultaneously[151]. The kinetic process parameters have been obtained (first reaction order, $\Delta H^{\neq} = 27.3$ kcal mol^{-1}, $\Delta S^{\neq} = -8$ e.u.[151], $\Delta G^{\neq} = 28.9$ kcal mol^{-1}, and $\lg A = 11.74$ [152]); it was shown[151] that the reaction proceeds at comparable rates in the liquid and gas phases. The 1,5-shift of hydrogen was considered as the reaction mechanism. This mechanism was subsequently confirmed by elegant experiments[152,153]. Thus the isomerisation of 7,8-dideuterocyclo-octatriene (LXII) [152] via the 1,5-hydrogen shift mechanism should lead to a redistribution of deuterium only between the 7(8)- and 3(4)-positions, while a redistribution of deuterium between all possible positions should correspond to the 1,3-shift of hydrogen. It has been established[152] that isomerisation results in the attainment of thermodynamic equilibrium between the trienes (LXII) and (LXIII) (isomer ratio 43.7 : 1 at 225 °C). The redistribution of deuterium takes place already at 180 °C, but even at 270 °C the label is located solely in the 3(4)- and 7(8)-positions:

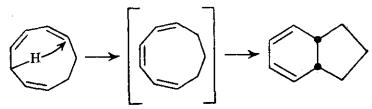


Analogous conclusions were reached in a study[153] of the thermal transformations of 5,8-dideuterocyclo-octa-1,3,6-triene as a result of the isomerisation of which the distribution of the label in the 1,3,5-triene formed also corresponds to 1,5-shift of hydrogen. The absence of hydrogen exchange between the molecules in both cases[152,153] confirms the intramolecular reaction mechanism. It has been established[152,153] that a high primary kinetic isotope effect ($k_H/k_D = 5.0$) corresponds to the isomerisation of cyclo-octatrienes with a slight secondary isotope effect (1.02–0.2). Thus the double bonds in cyclo-octatriene migrate via the 1,5-hydrogen shift mechanism.

It has been reported that the isomerisation of cyclo-octa-1,3-triene to the 1,3,5-isomer (mixed with its bicyclic valence tautomer) takes place in t-butyl alcohol in the presence of potassium t-butoxide (2 h, 90 °C) [148,149,154] or under the influence of an alcoholic solution of potassium hydroxide (4 h, 90–100 °C).[149] However, comparison with the thermal isomerisation conditions does not permit an unambiguous claim that in this case the process is vigorously catalysed by bases.

IX. CYCLONONATRIENES

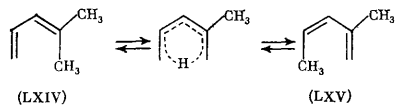
The thermal isomerisation of *cis,cis,cis*-cyclonona-1,3,6-triene to bicyclo[4,3,0]nona-2,4-diene at 200 °C was observed in 1963:[155]



The 1,5-shift of hydrogen was regarded as a hypothetical intermediate stage in the reaction[155].

X. ACYCLIC DIENES

The reversible thermal isomerisation of 4-methylpenta-1,3-diene (LXIV) to *cis*-2-methylpenta-1,3-diene (LXV) in the vapour phase at 350–450 °C (contact time ~1 s) has been described[156]:



It was concluded[156] that the transformation takes place via the 1,5-shift of hydrogen and the migration of two double bonds; a planar six-membered cyclic system was considered as the transition state in the reaction. *trans*-Dienes, incapable of forming a cyclic transition state (for example, *trans*-2-methylpenta-1,3-diene and *trans*-2,5-dimethylhexa-1,3-diene), are thermally stable. According to Wolinsky et al.[156], the (LXIV) + (LXV) equilibrium mixture contains ~80% of the diene (LXIV). Subsequently these results were reproduced[157] and it was shown that at 200 °C the equilibrium mixture contains 93% of compound (LXIV) and at 400 °C its content is 81%.

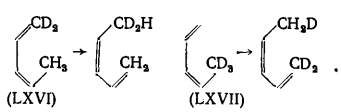
The kinetic data obtained for isomerisations of this type are presented in Table 4. In all the instances investigated the reaction is of first order and has an activation entropy characteristic of the 1,5-shift.

Table 4. Kinetic parameters of the 1,5-shift of hydrogen in the series of acyclic dienes (200–250 °C).

Compound	Reaction product	$\Delta G^{\neq}$, kcal mol^{-1}	$\lg A$	Refs.
2-Methyl-*cis*-penta-1,3-diene	4-methylpenta-1,3-diene	32.8	11.24*	[157]
2-Ethyl-*cis*-penta-1,3-diene	4-methyl-*trans*-hexa-1,3-diene	31.6	10.77	[159]
4-Methyl-*trans*-hexa-1,3-diene	2-ethyl-*cis*-penta-1,3-diene	34.5	11.03	[159]
cis-Hexa-1,3-diene	*cis, trans*-hexa-2,4-diene	32.5	10.80**	[160]
2,3-Dimethyl-*cis*-penta-1,3-diene	3,4-dimethylpenta-1,3-diene	33.8	11.13	[161]
3,4-Dimethylpenta-1,3-diene	1,3-dimethyl-*cis*-penta-1,3-diene	33.3	10.97	[161]

*$\Delta S^{\neq} \cong -8$ e.u.
**$\Delta S^{\neq} \cong -12$ e.u.

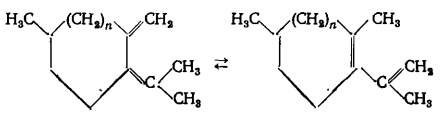
The thermal transformations of 1,1-dideutero- and 5,5,5-trideutero-*cis*-penta-1,3-dienes (LXVI) and (LXVII) have been investigated[158]:



The above reactions are not accompanied by hydrogen exchange between the molecules (intermolecular mechanism) and are not base-catalysed. Comparison of the results of kinetic measurements for the isomerisation of the diene (LXVI) ($\Delta H^{\neq} = 35.4$ kcal mol^{-1}, $\Delta S^{\neq} = -7.1$ e.u., migration of hydrogen) and the diene (LXVII) (migration of deuterium in the same system) led to $k_H/k_D = 12.2$, which agrees well with a cyclic highly symmetrical transition state.

Thus a typical 1,5-shift of hydrogen can occur in acyclic *cis*-diene systems with a chain length corresponding to more than 5 carbon atoms. We may note that the rate of isomerisation is close to that of cycloheptadienes.

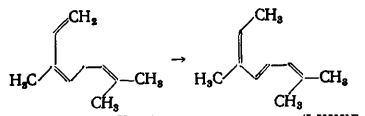
Isomerisation of a similar type also takes place in dienes with two exocyclic double bonds; for example, the reversible transformations (LXVIII)⇌(LXIX) and (LXX)⇌(LXXI) have been observed[156]:



(LXVIII), (LXX) (LXIX), (LXXI)

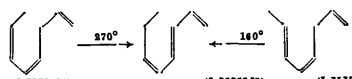
(LXVIII), (LXIX): $n = 0$ in equilibrium with ~80% (LXIX)
(LXX), (LXXI): $n = 1$ in equilibrium with ~90% (LXXI).

Two double bonds can migrate via the 1,5-shift mechanism in acyclic polyene systems; for example, the isomerisation of natural ocimene [3,7-dimethylocta-1,3,6-triene (LXXII)] to allo-ocimene [2,6-dimethylocta-2,4,6-triene (LXXIII)], which takes place at 160–190 °C, can be readily explained from these standpoints[162–164]:



(LXXII) (LXXIII)

It has been reported[165] that two double bonds in 6-*cis*,4-*cis*- and 6-*trans*,4-*cis*-octa-1,4,6-trienes (LXXIV) migrate with formation of octa-1,3,5-triene (LXXIV):

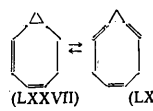


(LXXIV) (LXXVI) (LXXV)

The triene (LXXV) isomerises much more readily than its geometrical isomer (LXXIV) (at 160 °C instead of 270 °C) and the centres involved in the reaction are therefore distributed more readily in a single plane.

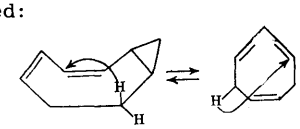
XI. HOMODIENYL SYSTEMS

Isomerisation of a similar type can occur in cyclic systems where one of the double bonds is replaced by a three-membered ring (homodienyl systems). It has been observed[151] that at 150–180 °C bicyclo[6,1,0]nona-2,4-diene (LXXVII) is converted into cyclonona-1,4,7-triene (LXXVIII):

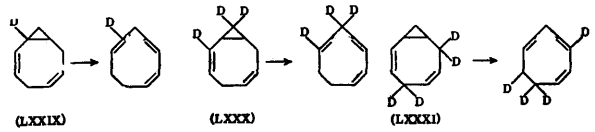


(LXXVII) (LXXVIII)

It has been established that this reaction is reversible; the equilibrium mixture contains 8–9% of compound (LXXVII). The 1,5-shift of hydrogen was considered as the reaction mechanism and the conformational proximity of the migration centres was noted:

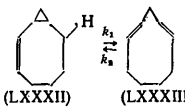


The isomerisation of bicyclo[6,1,0]nona-2,5-diene takes place similarly and the direction of the reaction (the 1,5-shift of hydrogen) has been convincingly confirmed by the study of the position of deuterium in the products of the thermal transformations of the three labelled compounds (LXXIX), (LXXX), and (LXXXI):[166]



(LXXIX) (LXXX) (LXXXI)

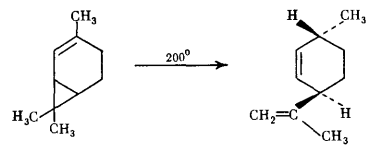
A similar reaction has been observed[146] in relation to bicyclo[6,1,0]non-2-ene (LXXXII) at 150–170 °C:



(LXXXII) (LXXXIII)

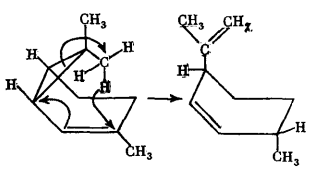
The equilibrium constant $K = k_1/k_2 = 82.3$. $\Delta H_1^{\neq} = 31.4$ kcal mol^{-1} and $\Delta S_1^{\neq} = -6$ e.u. have been obtained for the reaction (LXXXII) → (LXXXIII), which differs insignificantly from data for the 1,5-shift of hydrogen in the corresponding diene system. The rate constants for the isomerisation (LXXXII) → (LXXXIII) in the liquid and gas phases have similar values. The same isomerisation occurs[167] in *exo*-9-hydroxymethylbicyclo[6,1,0]non-2-ene at 240–340 °C, leading to the 3-hydroxymethylnona-1,4-diene. The 1,5-shift of hydrogen has also been observed in the bicyclo[5,1,0]oct-2-ene system (LXXXIV) at 180–300 °C, cyclo-octa-1,4-diene (LXXXV) being formed as a result of the reversible reaction[168]. The equilibrium constant $K = 36$; kinetic measurements led to $\Delta G^{\neq} = 38.6$ kcal mol^{-1} and $\lg A = 13.17$. It is noteworthy that a common feature of the 1,5-shift in homodienyl systems is the opening of the three-membered ring with formation of dienes containing isolated (1,4) double bonds†.

An interesting example of isomerisation in homodienyl systems with a six-membered main ring is provided by the transformations of 3,7,7-trimethylbicyclo[4,1,0]hept-2-ene (LXXXVI) (Δ^4-carene) and its derivatives into non-conjugated dienes [isolimonene (XXXVII)], which are rigorously stereospecific[174,175]:



(LXXXVI) ($a_D^{20} = +92.7°$) (LXXXVII) ($a_D^{20} = +119.5°$)

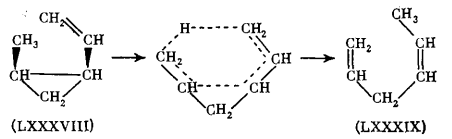
The kinetic parameters obtained for this reaction[174] are typical for the 1,5-shift of hydrogen: $\Delta H^{\neq} = 27.2$ kcal mol^{-1} and $\Delta S^{\neq} = -17.2$ e.u. The isomerisation of (+)-3-hydroxymethyl-Δ^4-carene is just as stereospecific[176]. Transformations of this type also evidently involve a transannular 1,5-shift of hydrogen, in which the hydrogen atom of the *endo*-methyl group in the 7-position, conformationally close to that of the second migration centre, is involved:



† In homodienyl systems with a smaller main ring (C_6 and smaller) the opening of the three-membered ring proceeds via a mechanism differing from the 1,5-shift[109,169–173].

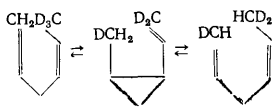
The absence of the 1,5-shift in homodienyl systems with a six-membered main ring but without an *endo*-substituent in the three-membered ring is probably due precisely to conformational factors or, in other words, to the remoteness of the hydrogen atom in the 5-position from the corresponding p-π-orbital of the double bond (in the 3-position).

In methylvinylcyclopropane systems the mechanism of the thermal transformations also depends on their configuration. Thus it has been established[177,178] that at temperatures above 160 °C *cis*-1-methyl-2-vinylcyclopropane (LXXXVIII) isomerises quantitatively to *cis*-hexa-1,4-diene (LXXXIX); under these conditions, *trans*-1-methyl-2-vinylcyclopropane is thermally stable:



(LXXXVIII) (LXXXIX)

The kinetic parameters of the reaction (LXXXVIII) → (LXXXIX) ($\Delta G^{\neq} = 31.2$ kcal mol^{-1} and lg $A = 11.03$ according to the data of Ellis and Frey[177] and $\Delta H^{\neq} = 30.2$ kcal mol^{-1} and $\Delta S^{\neq} = -11$ e.u. according to the data of Roth and Konig[179]) are satisfactorily consistent with the 1,5-hydrogen shift mechanism. This mechanism was subsequently convincingly confirmed[179] by a study of the thermal isomerisation of 6,6,6-trideutero-*cis*-hexa-1,4-diene (XV):

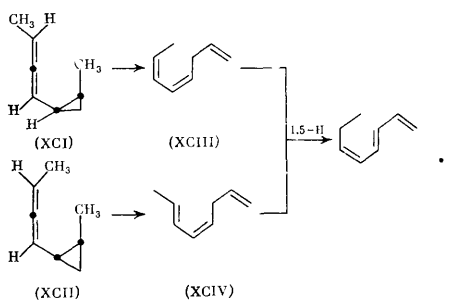


(XC)

The redistribution of deuterium between the terminal C atoms of the system can be accounted for in this instance solely by a reversible intramolecular 1,5-shift of hydrogen.

Thus the necessary and sufficient condition for the 1,5-shift of hydrogen in conjugated homodienyl systems is the coplanarity of the five C atoms which are potential participants in the reaction and the spatial proximity of the terminal C atoms in this system.

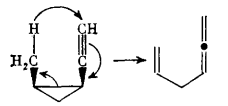
The 1,5-homodienyl shift of hydrogen has been observed recently[165] in compounds where the double bond is part of the allene system. One of the diastereoisomers of the substituted cyclopropylallene (XCI) readily isomerises in the form of a 5% solution in benzene at 125 °C to *cis*-octa-1,3,5-triene (XCIII), while the isomerisation of the other diastereoisomer (XCII) to the triene (XCVI) takes place at 160 °C at a much lower rate[165]:



(XCI) (XCIII)

(XCII) (XCIV)

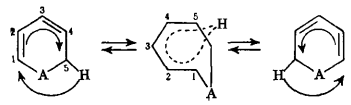
The only instance of the 1,5-shift in a system containing a triple bond is the thermal isomerisation of *cis*-2-ethynyl-1-methylcyclopropane above 350 °C; the initial product is hexa-1,2,5-triene[180]:



XII. GENERAL AND CHARACTERISTIC FEATURES OF THE REACTION AND ITS MECHANISM

The experimental data examined above show that the 1,5-shift of hydrogen or a substituent is an extremely common phenomenon in organic chemistry. This reaction is evidently characteristic of any *cis*-1,3-diene or polyene system including cyclic, acyclic, and homodienyl systems.

In general the 1,5-shift involves the displacement of a system of two double bonds to a neighbouring carbon atom (at the 5-position) and the migration of hydrogen (or a substituent) from this atom to the $C_{(1)}$ atom of the initial diene system:



(XCV)

Only the 1,3-diene system exhibits the ability to migrate, since it is well known that cyclohexa-1,4-diene[181] and cyclohepta-1,4-diene[182] do not undergo thermal isomerisation. In 1,4-dienes with C_9 and larger rings the 1,5-shift of hydrogen leads to the closure of a three-membered ring (to a slight extent as a reversible reaction). 1,4-Homodienyl systems are also thermally stable up to 500 °C, which has been established in relation to bicyclo[4,1,0]hept-3-ene[172] and 3,7,7-trimethylbicyclo[4,1,0]hept-3-ene.[175,183]

The migrating system of double bonds must have the *cis*-configuration, since the *trans*-dienes in the acyclic series (see above) as well as cyclic dienes with a fixed transoid system of double bonds do not enter into the reaction under consideration[74,96].

It has been established reliably for each of the cases discussed above that the thermal isomerisation proceeds precisely as the 1,5-shift and not the 1,3-shift, involving the migration of one of the double bonds; the latter would have led to a sequence of interconversions of isomers which has been reliably ruled out by experimental data.

In polyene chains or rings only two double bonds participate in the reaction, i.e. the thermal isomerisation involves the 1,5- and not the 1,7-shift. The migration of the alkoxy-group in the series of cycloheptatrienes (the 1,7-shift) is one of the few exceptions known at the present time.

Reactions proceeding via a stage involving the elimination of a proton, particularly in the series of cyclopenta-, cyclohexa-, and cyclohepta-dienes capable of forming the corresponding anions, can formally lead to the same final results as the 1,5-shift of hydogen (i.e. to the establishment of thermodynamic equilibrium between the isomers). However, in relation to such reactions the 1,5-shift has the following clear-cut distinctive features:

(1) The absence of hydrogen exchange in the isomerisation process (intramolecular mechanism).

(2) Comparable rates of reaction in the liquid and gas phases.

(3) A high (in absolute magnitude) negative entropy of activation ($\Delta S^{\neq} = -8$ – -12 e.u.).

(4) A high primary kinetic isotope effect $k_H/k_D \geq 6$ (for the migration of hydrogen).

(5) Stereospecificity of the reaction.

The above features of the isomerisation of diene and polyene systems make it possible to classify it unambiguously as the 1,5-shift.

The rate of isomerisation decreases in the sequence cyclopentadiene–cyclohepta-1,3-diene–cyclohexa-1,3-diene ($C_5 > C_7 \gg C_6$); comparison with the acidity sequence of hydrocarbons ($C_5 > C_6 \cong C_7$) shows that there is no charge separation in the transition state. This conclusion has also been confirmed by the weak dependence of the rate of reaction on the nature of the solvent and by the comparable rates of reaction in the liquid and gas phases. Thus the 1,5-shift is a process proceeding as a "reaction without a mechanism".

The transition state of the reaction is cyclic, rigorously ordered, and highly symmetrical, the migrating hydrogen atom being approximately equidistant from the migration centres (the 1- and 5-positions). This has been confirmed by the high negative entropies of activation for the reaction and the high primary kinetic isotope effect. This transition state corresponds to a synchronous shift of hydrogen and the double bonds. In the transition state the five carbon atoms participating in the reaction form a planar or almost planar system of the type of (XCV). A mechanism of this type is referred to as sigmatropic, since it is based on the migration of a σ-bonded hydrogen atom, which interacts in the transition state with the two ends of a 4π-electron system. The total number of electrons in the system constitutes a sextet, i.e. the most stable (according to the Hückel rule) system is formed. As a result of the reaction the π orbital of the carbon atom in the 1-position is converted into the sp^3-hybrid orbital of the new C–H bond, while the sp^3-orbital of the $C_{(5)}$–H bond is converted into the π orbital of the diene (polyene) system. A similar mechanism has been discussed in a number of studies[184–187] and has been confirmed by quantum-mechanical calculations[188].

From the standpoint of the conservation of orbital symmetry, considered in detail, for example, by Woodward and Hoffmann[187] and Gilchrist and Storr[189], the fact that the isomerisation of diene and polyene systems takes place as the 1,5-shift has been explained on the basis of selection rules. This mode of reaction is of the suprafacial type[187,189], i.e. the *s* orbital of hydrogen overlaps a lobe of the *p* orbital of carbon in the 1-position located on the same side of the plane; this overlap makes the given process allowed for the thermal reaction. In the same systems the 1,3- and 1,7-shifts should proceed via an antarafacial pathway with participation of the *p* orbital on the opposite side of the plane of the system. In the 1,3-shift such overlap requires a considerable angular strain in the molecule and it does not therefore occur under the conditions of the thermal reaction. For the 1,7-shift, the antarafacial pathway in the thermal reaction is in principle possible, but in this case the potential barrier to the reaction is much higher than for the 1,5-shift.

The velocity of the 1,5-shift of hydrogen in different systems varies within fairly broad limits. The reaction takes place most readily in cyclopentadienes ($\Delta G^{\neq} \cong 20$ kcal mol^{-1}) and with the greatest difficulty in cyclohexadienes ($\Delta G^{\neq} \cong 39$ kcal mol^{-1}); for cycloheptadienes as well as dienes and trienes with large rings, $\Delta G^{\neq} = 29$–31 kcal mol^{-1}. Presumably the above differences are associated with the distance between the $C_{(1)}$ and $C_{(5)}$ migration centres; in other words, the ease of isomerisation is determined by the conformational proximity of the $C_{(5)}$–H bond and the π orbital of the $C_{(1)}$ atom. Cyclopentadiene is known to have a planar conformation[190–192], the cyclohexa-1,3-diene molecule is almost planar[193], while the cyclohepta-1,3-diene[194] and cyclo-octa-1,3-diene molecules[50,195–197] are non-planar and have a large dihedral angle; for higher cyclodienes, a non-planar configuration is apparently also typical. An approximate estimate of the distances between the migration centres (the 1- and 5-positions) in cyclopenta-, cyclohexa-, and cyclohepta-dienes in the given conformations shows that, in terms of this distance, the cyclic dienes can be arranged in the sequence $C_5 < C_7–C_9 \ll C_6$, which is satisfactorily correlated with the sequence based on decreasing rates of isomerisation.

The 1,5-shift of substituents in all the cases investigated takes place under more severe conditions than the 1,5-shift of hydrogen; the greater the ease of migration of hydrogen in the given system, the greater the difference between the rates of migration of hydrogen and substituents. Evidently the shift of substituents takes place fundamentally via the same pathway as the shift of hydrogen. The lower rate of migration of alkyl groups is apparently due to the fact that the ability of the *s* orbital of hydrogen to form a "bridge"[189] bond in the transition state is greater than that of the sp^3-hybrid orbital of the alkyl group. The more pronounced *s* character of the sp^2-hybrid orbital in the phenyl group can account for the greater rate of its migration compared with that of the alkyl group.

In all cases the 1,5-shift of hydrogen is completed by the establishment of thermodynamic equilibrium between the isomers with respect to the position of the system of endocyclic double bonds. The composition of the equilibrium mixture is determined by the operation of thermodynamic factors alone. Two limiting cases are possible in principle: (1) if the difference between the free energies of the isomers is close to zero, their concentrations in the equilibrium mixture are practically equal; examples of such mixtures are provided by deutero-derivatives of dienes and polyenes; (2) if one of the isomers is much more favoured by energy factors ($\Delta\Delta G > 1.5$ kcal mole^{-1}), than its concentration in the equilibrium mixture is close to 100%; examples of such systems are provided by 1,2,3- and 1,2,4-trimethylcyclopentadienes (see above).

Comparison of the compositions of the equilibrium mixtures in different series revealed general features; (a) a lower stability of isomers containing a substituent in the methylene groups; (b) comparable thermodynamic stabilities of isomers differing in the position of an alkyl group attached to the system of double bonds; (c) the fact that isomers containing a substituent which lengthens the conjugation chain inthe 1-position are preferred. These features should apparently hold for the substituted *cis*-dienes which have not yet been investigated.

For cyclic diene systems, the main contribution to the difference between the free energies of the isomers comes from the entropy factor. Hence one may conclude that the composition of the equilibrium mixtures of cyclic dienes and polyenes should vary insignificantly within wide temperature limits, since the temperature dependent term in the equation defining the equilibrium constant is either small or close to zero. The temperature dependence of the composition of the equilibrium mixtures has been hardly investigated, but comparison of the ratios of the isomeric 1,2,3,4-, 1,2,3,5-, and 1,2,4,5-tetramethylcyclopentadienes at 20 °C (79 : 10 : 11)[21,77] and 500 °C (79 : 5 : 16)[77] confirms this hypothesis.

Systems in which there is a possibility of a 1,5-shift of hydrogen or a substituent are naturally not exhausted by those listed above. Presumably transformations of this type will be discovered in the immediate future for other representatives of the class of *cis*-diene and polyene structures, including homodienyl structures. In particular, the 1,5-shift of substituents, especially functional groups, has been virtually uninvestigated for systems with more than seven carbon atoms in the ring.

In conclusion one should note that the possibility of a 1,5-shift, particularly the 1,5-shift of hydrogen, should be taken into account in the study of any chemical reactions of dienes and polyenes.

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Metallotropic Tautomeric Transformations of the σ,σ-Type in Organometallic and Complex Compounds

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The review is devoted to the consideration of studies in the field of metallotropy—a new type of tautomeric transformations of organometallic and complex compounds involving the intramolecular and intermolecular migration of metal-containing groups.
The bibliography includes 221 references.

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I. INTRODUCTION

The problems of tautomerism constitute one of the most important branches of theoretical chemistry and have attracted the constant attention of investigators throughout many years. The foundations of the science of tautomerism were laid as early as the end of the past century by A.M.Butlerov. Until the end of the 1950's, the most thoroughly investigated type of tautomerism involved prototropic transformations accompanied by the dissociation of σ-bonds and the migration of the hydrogen atom between cation-accepting centres. The study of these processes enabled M.I.Kabachnik to create a quantitative theory of prototropic equilibrium.

At the beginning of the 1960's a qualitative jump occurred in the study of tautomerism. It was caused, on the one hand, by the discovery of tautomeric processes associated with the dissociation of donor–acceptor σ- or π-bonds and processes involving the migration of groups containing a metal, metalloid, or carbon key atom and, on the other hand, the extensive application of the NMR method. All these factors led to the vigorous accumulation of qualitatively new facts and to the development of fundamentally new ideas in the theory of tautomeric processes.

This review deals with studies in the field of metallotropic transformations of organometallic and complex compounds. If the phenomenon under consideration is defined more vigorously, then one must assume that metallotropic transitions occur as a result of a change in the relative positions of two fragments of the compound—cationoid and anionoid, accompanied by the dissociation of some bonds and the formation of others between the metal and the ligand and in many instances also by a redistribution of the multiple bonds of the latter. Here the cationoid residue may be the metal or the organometallic group or another metal-containing species, where the metal forms a bond with the anionoid residue before and after the metallotropic transition. The anionoid residue can consist of a bifunctional (in the general case a polyfunctional) ligand capable, in principle, of forming several variants of the chemical bond with the same metal atom of the cationoid residue.

Initially[1-17] the problem of metallotropy was formulated and solved in relation to derivatives of prototropic tautomeric systems in which a "mobile" hydrogen atom has been replaced by an organometallic group. Among other features, in these studies the specific characteristics of the phenomenon, associated with the replacement of H by MR_n, were discovered. It was found that metallotropic systems are in all cases analogues of the corresponding prototropic models (as regards their structure and the process mechanism) and have many interesting, frequently fundamental, characteristic features.

It was subsequently discovered that, in principle, metallotropic transitions can occur in systems of very many types, including those very remote from the prototropic analogues. In particular, various types of metallotropic transformations in π-complexes of transition metals have been observed and in many cases investigated in detail.

If this classification of the phenomenon of metallotropy is based on the nature of the bond formed by the metal, it is possible to distinguish three main types of metallotropic transitions: σ,σ- transitions, π,π-transitions, and σ,π-transitions. For tautomeric transformations of the σ,σ-type (sigmatropic transitions), it is postulated that before and after the rearrangement the metal forms localised (principle-valence or coordinate)σ-bonds with topologically different atoms of the anionoid residue of the given or another molecule. Transitions of the π,π-type consist in the migration of the metal from the system of multiple bonds, with which the π-bond had been formed initially, to a topologically different system in the given or another similar molecule. For transitions of the σ,π-type, it is suggested that in the initial and final states the metal forms bonds of different types with the ligand. The metallotropic π,π- and σ,π-transitions do not have prototropic analogues, while many (but not all) σ,σ-transitions are formally analogous to the corresponding prototropic systems. Studies on metallotropic π,π- and σ,π-transformations have been reviewed[18]. This review therefore deals mainly with the advances in recent years in the study of sigmatropic transitions of metal-containing groups.

A particular feature of the phenomenon considered must be emphasised. Metallotropic transitions can occur not only intramolecularly but are frequently also intermolecular. We shall adopt the convention that the intramolecular transformations are those in which the cationoid metal-containing group migrates between atoms of the same anionoid residue and which are not accompanied by the decomposition of the

given compound into kinetically independent species. On the other hand, in intermolecular metallotropic transitions the metal-containing species is separated for a short time from the anionoid residue and is attached to a "transferring agent" or passes into the bulk of the solution, as a result of which after the metallotropic transition the cationoid species is bound not to its "own" anionoid residue but to a "foreign" one. In terms of purely external features, the intermolecular metallotropic transitions may not differ from exchange processes in which the metal-containing species migrates from one anionoid residue to another. We shall therefore adopt the convention that metallotropic transitions will be assumed to be only those where the intermolecular migrations of the cationoid residues take place between bifunctional or polyfunctional ligands [process (I)]; and henceforth the symbol [M] denotes a metal-containing species, its organoelemental analogue, or a proton (cationoid residue), which is bound via the M–E σ-bond to the anionoid residue [E]. On the other hand, the transitions of metal-containing species between monofunctional ligands will be classified as exchange reactions [process (II)]:

$$[M]-[E]-\rightleftarrows [M]-[E^*]- \quad (1)$$
$$[E^*]- \qquad\qquad [E]-$$

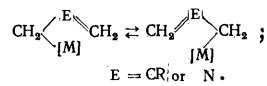
$$[M]-[E]+[M^*]-[E^*] \rightleftarrows [M]-[E^*]+[M^*]-[E]\,. \quad (2)$$

Mainly infrared and ultraviolet spectroscopic methods were used initially in studies of metallotropy and the equilibrium position in metallotropic systems[1–8]. However, subsequently high-resolution NMR, particularly dynamic NMR, began to be used on a wider scale for these purposes[9–17]. With the aid of the latter, it is often possible to obtain the kinetic characteristics of metallotropic processes, which permits a successful analysis of their mechanisms. This is because metallotropic transitions, like tautomeric transformations in general, frequently take place at rates comparable to the NMR time scale, which makes it possible to investigate not only the ratios of the possible tautomers but also the dynamics of their transformations. In view of these factors, a further consideration of the phenomenon of metallotropy will be based mainly on NMR results, but if necessary other data will also be employed.

The first experimental evidence in support of the occurrence of metallotropic transitions in organometallic compounds of non-transition metals was apparently obtained in 1960 by Nasmeyanov and Kravtsov[1] in an infrared and ultraviolet spectroscopic study of solutions of arylmercury derivatives of *p*-nitrosophenols in aprotic media. In a series of subsequent studies other instances of the migration of metal-containing groups between carbon atoms or heteroatoms of the corresponding molecule were investigated or simply discovered: however, one should note that these studies, including those by NMR, have been by no means systematic for all the models; the review of the relevant studies is therefore unfortunately somewhat fragmentary. In order to overcome this deficiency to some extent, in the analysis of certain model structures, for which the migration of metal-containing groups is as yet unknown, has been little studied, or may be impossible, we considered instances of E,E-transitions (E = C,N,O,S,etc.) with participation of cationoid species such as SiR_3 and GeR_3, which are organoelemental analogues of the groups R_3Sn and R_3Pb, as well as organometallic groups involving transition and light non-transition metals.

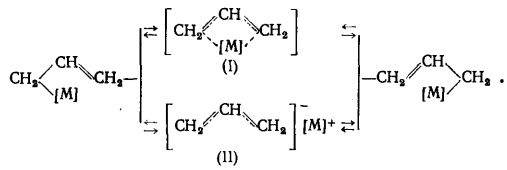
II. METALLOTROPIC C,C-TRANSITIONS

Among "purely carbon" systems, where there is a possibility of C,C-transitions of metal-containing groups accompanied by the dissociation of old and the formation of new metal–carbon bonds, one must first consider the simplest three carbon system $-\underset{|}{\overset{|}{C}}-C=C-$, whose prototropic analogue has a
[M]
relatively low mobility (as well as the related azomethine triad $-\underset{|}{\overset{|}{C}}-N=C-$ with a central nitrogen atom, which has not been
[M]
investigated at all from the standpoint of metallotropic transitions):



(3)

Although the occurrence of metallotropic 1,3-transitions [reaction (3)] with E=CR has usually been considered for a fairly wide range of allyl derivatives, we believe it is correct to discuss here only those examples in which the existence under specific conditions of a localised C_3H_5–[M] σ-bond has been demonstrated reliably. When the migration is retarded by the protons of the allyl group, the ^1H NMR spectrum shows the corresponding $AKLX_2$ system, which in a case of sufficiently rapid intramolecular or intermolecular C,C-transitions [reaction (4)], involving the C–M bond, degenerates to AX_4 (the corresponding spin systems are observed also for substituted allyl radicals). This phenomenon has been observed, in particular, in NMR studies of the compounds C_3H_5HgX[19,20], $(C_3H_5)_2Zn$[21,22], and $(C_3H_5)_3B$[23]:

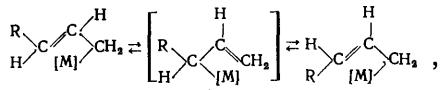


(4)

It has been suggested that the 1,3-transitions [reaction (4)] take place with the intermediate formation of either the transition state (I) or of ionic structures, for example of type (II). In the case of $(C_3H_5)_2Zn$[21,22] and asymmetric allyl derivatives of mercury[19,20], reaction (4) is intermolecular and that involving allyl derivatives of boron is intramolecular[23].

The occurrence of process (4) was first postulated in an attempt to explain the NMR spectra of allyl derivatives of magnesium[24]. However, one should note that the spectral pattern corresponding to the inhibition of the metallotropic transition has not so far been observed in the NMR spectra of the asymmetric derivatives C_3H_5MgX and $RCH{=}CHCH_2MgX$ even at very low temperatures[21–30], so that the question of the occurrence of migration processes in these systems has in essence remained open. In the study of the ^1H NMR spectra of the asymmetric compound $(t\text{-}C_4H_9CH_2CH{=}CHCH_2)_2Mg$ it was shown recently[31] that, at sufficiently low temperatures, both the *cis*- and *trans*-forms of this compound with C–Mg σ-bonds exist simultaneously in solvating media, while at higher temperatures they undergo an interconversion. These results suggested that the *cis–trans* isomerisation [reaction (5)] is preceded by the formation of structure (III)

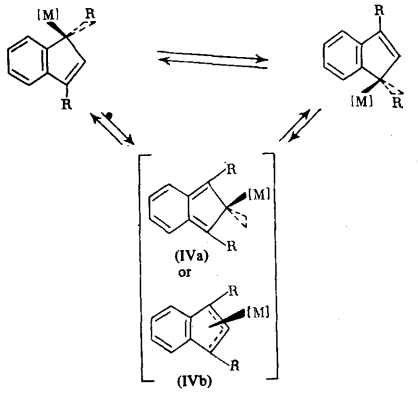
for a short time, evidently as a result of the metallotropic 1,3-transition



(III)
R = t-$C_4H_9CH_2$ (5)

where [M] = $MgCH_2CH{=}CHCH_2C(CH_3)_3$.

The indenyl organometallic compounds in which the C,C-metallotropic transformations [reaction (6)] can proceed not only via 1,3-transitions but also via two consecutive 1,2-shifts with formation of the intermediates (IVa) or (IVb), are an unusual example of a carbon triad:



(IVa) or (IVb) (6)

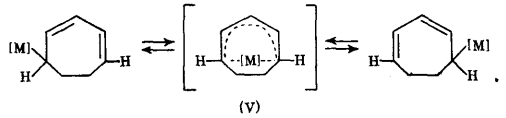
Changes in the ^1H and ^{13}C NMR spectra consistent with metallotropic C,C-transitions [reaction (6)] have been observed in the study of $(C_9H_7)_2Hg$,[10,32] $C_9H_7Sn(CH_3)_3$,[12,33-35] and other indenyl compounds[12,35-37], and it has been shown for a series of derivatives that this process takes place intramolecularly. The available NMR data for metallotropic transitions (6) indicate the dependence of the rate on the nature of [M] and make it possible to set up series based on the relative ease of metallotropic transformations as a function of the nature of the metal [series (7)] and the nature of the substituents in the group [M] [series (8)][35,38]:

$$R, H < Si(CH_3)_3 < Ge(CH_3)_3 < Sn(CH_3)_3 < HgC_9H_7; \quad (7)$$

$$Si(OCH_3)_3 < SiCl_3 < Si(CH_3)Cl_2 < Si(CH_3)_2Cl < Si(CH_3)_2C_6H_5 < Si(CH_3)_3. \quad (8)$$

As regards the mechanism of C,C-transitions (6), the results of the vast majority of the experimental and theoretical[39-41] studies support the view that they do not involve a 1,3-shift but proceed via consecutive 1,2-transitions. In particular, comparison of the energy characteristics of the C,C-transitions in indenyl and cyclopentadienyl (see below) organometallic compounds shows that in all cases the transition from $C_5H_5[M]$ to $C_9H_7[M]$ is accompanied by an increase of E_a by approximately 8.5 kcal mol^{-1}.[35] Bearing in mind that this quantity is close to the difference between the energies of the indenyl and isoindenyl structures, amounting to approximately 9 kcal mol^{-1} according to estimates[42], one can assume that the metallotropic transitions in indenyl derivatives take place via two consecutive 1,2-shifts with the intermediate formation of compound (IVa) or (IVb), which are not detectable by NMR.† Among other pieces of evidence in support of this mechanism, we may point to NMR data[12] for indenyl derivatives of tin with [M] = $Sn(CH_3)_2C_6H_5$ (R = H or CH_3). The authors[12] found that, in the absence of a dynamic system, the signals corresponding to the two CH_3Sn groups in [M] are shielded in different ways and can merge when the C,C-transitions are accelerated with increase of temperature. They interpreted this result as proof of the mechanism with a 1,2-shift, within the framework of which the intermediates (IVa) and (IVb) have a mirror symmetry plane, transforming one CH_3Sn group into the other, which is consistent with the averaging of their shielding (in the case of the 1,3-transition with inversion at the metal atom the two CH_3Sn groups should remain non-equivalent). The authors[12] noted, however, that the less probable 1,3-transition, with retention of the configuration at the tin atom and inversion of that at the asymmetric carbon atom, is also consistent with the experimental facts.

The occurrence of metallotropic C,C-transitions in allyl and indenyl derivatives is promoted by, among other things, appropriate geometrical factors. The detection of metallotropic transitions between more remote carbon atoms, particularly in pentad systems of type (9), is therefore important. The possibility of such transitions has been confirmed in an NMR study of the corresponding R_3Sn derivatives ($R = CH_3C_6H_5$).[49,50] The averaging of the shielding of the indicator nuclei in the 1- and 5-positions, associated with the acceleration of the C,C-transitions (9) via the 1,5-migration mechanism, apparently with the intermediate formation of the transition state (V), has been observed at fairly high temperatures in the ^1H and ^{13}C NMR spectra:

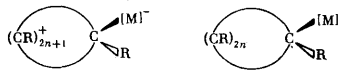


(V) (9)

The carbon systems with C,C-transitions (4), (6) and (9) can be conventionally referred to as "open" (in the sense used here they can evidently include also cyclic structures), because only "vibrational" transitions between two or more cation-accepting centres (degenerate or non-degenerate) are possible in them. Metallotropic systems of the "closed" type, in which there is a possibility of not only "vibrational" C,C-transitions but also of migrations of organometallic groups accompanied by the formation of a C–M bond in succession with all the carbon atoms of the system, have also been widely investigated. There is no point in considering the

† In making a choice between the two possible intermediates—the isoindenyl intermediate (IVa) and the π-allyl intermediates (IVb), one should apparently resort to the available NMR or other data concerning the structure of the σ-allyl derivatives of mercury, tin, germanium, and silicon[43-47]. Since tautomeric 1,3-transitions in these derivatives, accompanied by the intermediate formation of the π-structure (IVb), are unknown under non-catalytic conditions (the energy characteristics of the 1,3-transition in the π-allyl derivatives of silicon[48] show that the process is a rearrangement and not a tautomeric transformation), it is logical to give preference to the isoindenyl intermediate (IVa) when the 1,3-migration in indenyl organometallic compounds is considered.

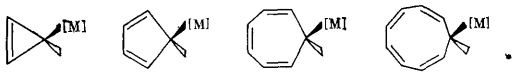
prototropic analogues of the "closed" systems because the relevant processes in such systems are clearly slow:



(VI) (VII)

(a) $n=1$, (b) $n=2$, (c) $n=3$, (d) $n=4$.

In the simplest "closed" systems the occurrence of metallotropic C,C-transitions appears to be most probable in even derivatives of type (VI) and in odd derivatives of type (VII).[18] Among structures (VII), σ-cyclopropenyl compounds (VIIa) ($n=1$, carbon triad) have so far not been investigated at all and the C,C-migration in σ-cycloheptatrienyl derivatives (VIIc) ($n=3$) and σ-cyclononatetraenyl derivatives (VIId) ($n=4$, R=H) of non-transition metals has been studied by NMR only for individual examples of organotin compounds[16, 50-52]. Thus the greatest number of publications deal with C,C-transitions in σ-cyclopentadienyl and related compounds (VIIb) ($n=2$, R=H or R≠H; carbon pentad)[11,32,35,41,53-81] (see also the relevant reviews concerning this problem[41,82,83]). The even charged structures (VI) have so far been investigated for the case with $n=1$ ($R=CH_3$)[84-86]:



(VIIa) (VIIb) (VIIc) (VIId)

The first convincing evidence in support of the occurrence of C,C-metallotropic transitions in σ-cyclopentadienyl compounds was obtained in 1965–1966 in a low-temperature NMR study of σ-cyclopentadienyl derivatives of iron[53], silicon, and germanium[54]. Subsequently analogous results were obtained in studies of compounds of a number of non-transition and transition metals[11,32,35,42,55-81]. In the ^1H NMR spectra of the C_5H_5 ligand in these compounds at fairly low temperatures a multiplet of the type AA'BB'X (or ABCDX for compounds with a lower symmetry) has been observed. The corresponding set of signals has been noted also in the ^{13}CNMR spectra. These results are consistent with the presence of a localised C_5H_5–M bond and have been confirmed in many instances in structural studies by diffraction methods[54, 59,87,88]. With increase of temperature, a number of patterns of an intermediate type are observed in the spectra and at still higher temperatures there is a single signal corresponding to the situation where all five ^1H or ^{13}C ring nuclei are equivalent as a consequence of the time averaging of their shielding.

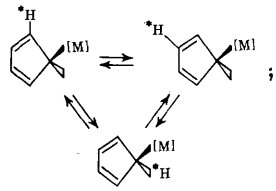
The change in the structure of the cyclopentadienyl compounds (VIIb) has an appreciable effect on the rates of metallotropic transitions in them. In particular, data referring to the derivatives of Group IVB elements[35,38,77] established the series (10)–(12) based on the relative changes in the rates of the processes as a function of the structure [M], which coincide with the corresponding series (7) and (8) established for indenyl organometallic derivatives:

$$R < Si(CH_3)_3 < Ge(CH_3)_3 < Sn(CH_3)_3, \quad (10)$$

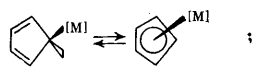
$$SiCl_3 < Si(CH_3)Cl_2 < Si(CH_3)_2Cl < Si(CH_3)_3, \quad (11)$$

$$Ge(OCH_3)_3 < GeCl_3 < Ge(GH_3)_3. \quad (12)$$

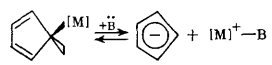
Three mechanisms for the migration of the organometallic group, leading to the averaging of the shielding of the nuclei in the NMR spectra, have been proposed: the intramolecular mechanisms (13) and (14) and the intermolecular mechanism (15) in highly basic media. Piper and Wilkinson[91], who were the first to suggest the possibility of sigmatropic C,C-transitions of the organometallic group in σ-cyclopentadienyl compounds of metals, pointed out that these transitions can proceed via the intramolecular migration of the metal along the perimeter of the ligand [reaction (13)]. Subsequently mechanism (14), postulating that the type of the C_5H_5–M bond changes in the course of intramolecular metallotropic transitions (σ,π-transitions[52]), was also proposed. Each of these mechanisms is consistent with the fundamental characteristics of the NMR spectra. The study of more detailed changes in the spectrum showed that the 1,2-shift mechanism (13) is preferable for intramolecular processes[53,60,61,92]; it presupposes the migration of the metal via the shortest path to a neighbouring carbon atom (and constitutes, as it were, a form of σ,π-conjugation: the opposed dynamic movement of electrons and the organometallic species). However, the available experimental data[52,63] do not allow the possibility of mechanism (14) to be rejected. The Woodward–Hoffmann rules have been extended to the study of the mechanism of sigmatropic migration in derivatives (VIIb)[39-41]:



(13)



(14)



(15)

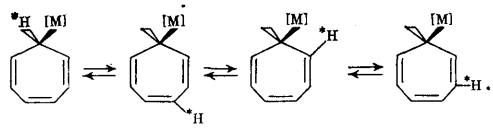
Certain factors complicating the analysis of the NMR spectra of the compounds C_5H_5–M must be emphasised. Firstly, in the study of the properties of cyclopentadienyl compounds of different metals the presence of the C_5H_5–[M] σ-bond is as a rule postulated in an explicit or implicit form (if, by virtue of its "electronic requirements", the metal can, in principle, form an M–C σ-bond) and hence a σ,σ-mechanism of the migration of metal-containing groups. However, the available data show that such hypotheses cannot be regarded as sufficiently correct in the absence of additional unambiguous confirmation (for example, the observation in the low-temperature ^1H NMR spectra of compounds C_5H_5-M of the spin system AA'BB'X, the observation of a localised bond in the study of compounds by diffraction methods, etc.). Secondly convincing evidence for the intramolecular character of the C,C-transitions of organometallic groups has been by no means obtained in all cases (the intramolecular nature of the transitions has been established, for example, for σ-cyclopentadienyl derivatives of Group IVB elements—Si, Ge, and Sn#)[35,62,69-73]. There are also more general difficulties associated with the existence of additional factors: the possibility of a change in the nature of the C_5H_5–M bond under the influence of solvents with a high solvating capacity[93-96], the ability of the cyclopentadienyl ligand to participate in the formation of a bridge bond with certain metals[97], the possibility of the retention of dynamic features in the C_5H_5–M fragment, even in a crystal[98], etc.

The fact that in organometallic derivatives of the type C_5H_5–M (in those compounds where the presence of a C,M σ-bond has been confirmed and in which the C,C-transitions

It has recently been found[92] that in highly basic media organotin groups can migrate also via the intermolecular mechanism (5).

are intramolecular) the existence of 1,2-transitions has been demonstrated led to an interesting theoretical problem. Indeed, among derivatives of type (VII) the mechanism of the C,C-migration satisfies two conditions simultaneously only in compounds (VIIb)—the intuitive idea that migration to the nearest atom (the 1,2-shift) is preferred and the orbital symmetry conservation rules (satisfied when the C,C-transition takes place via the 1,5-mechanism), because the 1,2- and 1,5-transitions are identical only in cyclopentadienyl compounds (VIIb).

Because of this, C,C-transitions have been investigated in some studies[16,50,99] in compounds (VIIc) with [M] = $Sn(C_6H_5)_3$, for which the 1,2- and 1,5-transitions do not coincide and can be fully distinguished by dynamic NMR:



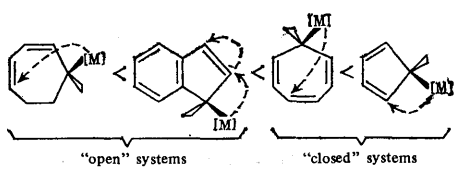
(16)

At low temperatures the ^1H and ^{13}C NMR spectra of this derivative correspond to a fixed structure with a localised C–M bond, which is consistent with data obtained in a study of this compound by a diffraction method in the crystalline state[99]. At higher temperatures the ^1H NMR spectrum shows a single signal corresponding to the seven protons of the cycloheptarrienyl ring with averaged chemical shifts. Analysis of the temperature-induced changes in the form of the NMR line led to the conclusion that the C,C-transitions within the limits of the seven-numbered ring take place via the 1,5-shift mechanism (16). Structure (VIII) has been proposed as a transition state in this process[49]. The possible formation of the centrally symmetrical structure (IX), at least at temperatures not exceeding 30 °C, has been rejected[16] on the grounds that the changes in the ^1H NMR spectrum are asymmetric. Thus the C,C-transitions of the organometallic group in derivatives (VIIc) do not take place in the direction of the shortest pathway (as in cyclopentadienyl compounds) but in the direction predicted by symmetry conditions. We may note, however, that, according to ^{13}C NMR data, the C,C-migrations of the organotin group in the σ-cyclononatetraenyl derivatives (VIId) take place preferentially in the direction of the shortest pathway[51].



(VIII) (IX)

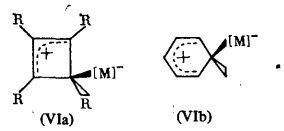
Summarising the data obtained hitherto for the C,C-transitions of organotin groups, we may quote the series (17), formulated by Curtis and Fink[49] and based on the increasing rates of metallotropic transformations as a function of the structure of the anionoid hydrocarbon residue:



"open" systems "closed" systems (17)

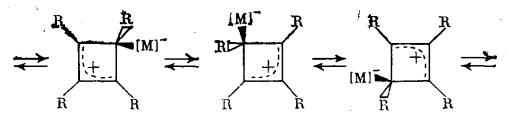
We may note that in all cases these are in essence sigmatropic 1,5-transitions (in terms of the classification of Woodward and Hoffmann[100]). In addition, the fact that the transitions in these systems are, from the point of view of their velocities, rearrangements rather than tautomeric transformations considered here when [M] = H appears to be significant. Thus the migration of organometallic groups in the systems analysed is promoted by additional factors, as a result of which the potential barrier is lower for heavier cationoid species. The principal factor appears to be the greater length of the C–M bond compared with the C–H bond and the presence in the metal atom of a vacant orbital, which is larger and has a lower energy than the potentially active vacant 2p orbitals of the hydrogen atom[101,102].

An analysis carried out as above in relation to the odd structures (VII) is in principle possible also for the even charged structures (VI):



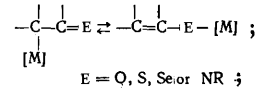
(VIa) (VIb)

Such analysis has been carried out hitherto only for the σ-complexes of cyclobutadiene–structure (VIa), $n = 1$, $R = CH_3$, $[M] = AlCl_3$.[84–86] Analysis of the ^1H and ^{13}C NMR spectra of the corresponding compounds over a wide range of conditions enabled a number of investigators[79–81] to find that in this case the intramolecular dynamics involves mainly (if not exclusively) the 1,2-shifts of the group $AlCl_3$ along the ring perimeter;



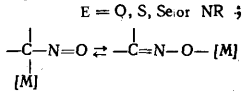
III. C,E-TRANSITIONS (E = O, S, Se, or NR)

Among non-degenerate C,E-triads, for which there is a possibility of the observation of metallotropic transitions, we shall point to two which are of particular interest—of the keto-enol type (18) and the nitroso-isonitroso type (19). In the corresponding non-metallated systems the reversible equilibrium prototropic transitions, which are rapid in terms of the NMR time scale, are as a rule observed extremely rarely[103]. However, in the study of the C,E-transitions in similar triads by procedures including the NMR method, certain advances have already been made, although in each individual case there is a probability of a shift of equilibrium (18) to one side, which precludes the simultaneous observation of both tautomeric forms in solution;



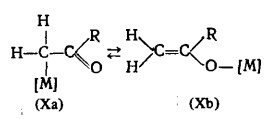
(18)

E = O, S, Se or NR;



(19)

The results of studies of keto-enol transformations (18) by procedures including infrared and NMR spectroscopy have been reported[14,104,105] for $[M] = R_3Sn$, R_3Ge, and E = O. The ratio of the tautomers in these systems depends on a number of factors, including the solvent and the presence of catalytic admixtures of certain compounds:

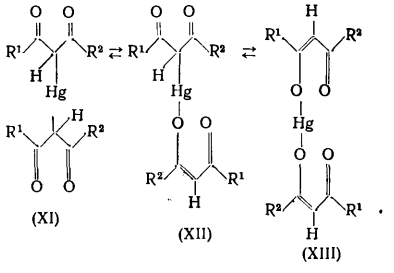


(Xa) (Xb) (20)

In the study of the ^1H NMR spectra of the $(CH_3)_3Sn$ derivative of acetone (X, $R = CH_3$)[14] the averaging of the signals due to the CH_2 groups of the O- and C-isomers was observed even in the absence of the catalysts, which indicates the

occurrence of fairly rapid C,O-transitions of the group $(CH_3)_3Sn$. The observed changes in the chemical shifts of the signals due to the CH_2 protons as a function of temperature permitted the conclusion that a change of temperature entails a displacement of tautomeric equilibrium (20) in the compound. The merging of the signals corresponding to different isomers and observed separately at lower temperatures has also been observed at 150 °C in chlorobenzene in the spectrum of the analogous derivative of acetophenone (X, $R = C_6H_5$).

C,O-Transitions of organomercury groups have been studied in connection with the analysis of the NMR spectra of a series of acetylacetonato-derivatives of mercury[15,106,107]:

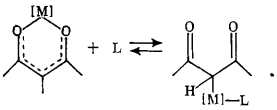


(21)

A study[15] of the keto-compound (XI, $R^1 = R^2 = t\text{-}C_4H_9$) in $CHCl_3$ showed that at room temperature the ^1H NMR spectrum does not exhibit signals corresponding to the $^{199}Hg-C-^1H$ spin–spin interaction, while at lower temperatures not only these satellites but also the methylidyne signal, corresponding to approximately a 3% content of one of the enol isomers (XII) or (XIII), are observed. This result can be explained by postulating that the organomercury group undergoes fairly rapid metallotropic C,O-transitions (21) in solution [in the crystal the compound exists only in the keto-form (XI)[106,108]]. It was subsequently found that[10] the C,O-transformations in this system are rapidly accelerated when ethanol-d_6 is used as the solvent.

A quantitative study of the keto–enol transitions (21) has been carried out[107] by dynamic NMR with the acac derivative of mercury, in which a high stabilisation of the enolic form ($R^1 = n\text{-}C_3F_7$ and $R^2 = t\text{-}C_4H_9$) has been achieved by introducing the electronegative group $n\text{-}C_3F_7$§. Apart from the main isomer (XI) in solution [in the crystal the compound exist only in the keto-form (XII)] comparable amounts have also been found of the enolic isomer (XII) and under certain conditions the two isomers are interconverted at a fairly high rate [isomer (XIII) with $R^1 = n\text{-}C_3F_7$ and $R^2 = t\text{-}C_4H_9$ is not formed, which facilitated the interpretation of the results by the authors[107]].

Analysis of the ^1H NMR line form of the compound in deuteroacetone in the temperature range from −60 °C, where the spectrum shows only the signal due to the proton of the methylidyne group of the keto-form (XI) and two signals due to the methylidyne protons of the enolic form (XII), to +40 °C, where all three signals merge into one, made it possible to determine the necessary thermodynamic parameters of the process ($E_a = 9.9$ kcal mol^{-1}).[107] Special experiments established that the metallotropic C,O-transitions take place intramolecularly in this instance (at least in the temperature range from −60° to +10 °C). It was noted that a change in the nature of the solvent influences the rate of the C,O-transitions but has almost no effect on the equilibrium position. Finally, analysis of the NMR data available for the acac derivatives of other metals capable of forming a C–M bond (platinum[110] and gold[111,112]) enabled the authors[107] to conclude that, among these metals, mercury is the most labile in relation to metallotropic C,O-transitions:

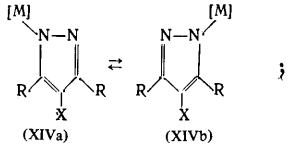


(22)

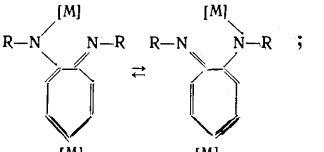
It has recently been reported[113] that the C,O-transition (22) has been detected by NMR in acetylacetonato-derivatives of gold with $[M] = Au(CH_3)_2$ and $L = PR_3$, in the course of which the acac ligand behaves either as a bidentate O-derivative or as a monodentate C-derivative. Reaction takes place when phosphines, which are necessary for the retention of the coordination number of the metal in the course of the process, are added to the solution.

IV. N,N-TRANSITIONS IN TRADITIONAL TAUTOMERIC SYSTEMS

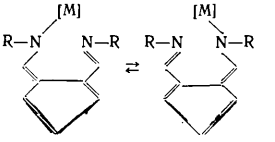
Among the traditional structures in which metallotropic N,N-transitions are possible, in principle, we may point in the first place to several even systems—the diad system (23), the tetrad system (24), and the hexad system (25).



(23)



(24)



(25)

Hypotheses concerning the possibility of the tautomeric transformations (23)–(25) for $[M] = H$ have been frequently put forward on the basis of various considerations including NMR data[114–122]. In particular, it has been possible[116] to "freeze" by dynamic NMR the prototropic N,N-transitions (25) and to discover the asymmetric structure of the fragment N...H–N. However, in terms of the phenomenon considered here the study of the N,N-transitions of the cationoid species $[M] \neq H$ has been developed to a definite extent only in the field of pyrazoles (23).

The occurrence of metallotropic N,N-transitions (23) has been demonstrated[17] in relation to *N*-arylmercury derivatives of pyrazoles and also[123–125] for $[M] = SiR_3$ and $Ge(CH_3)_3$. The case with $[M] = Sn(C_4H_9\text{-}n)_3$ has also been investigated recently[126].

N-Phenylmercury derivatives of 3,5-dimethyl-4-X-pyrazoles (XIV), where $[M] = HgC_6H_5$, $R = CH_3$, and X = Cl, Br, or NO_2, have been chosen[17] as model systems and the corresponding non-metallated compounds with $[M] = H$ were used

§ It must be emphasised that the acac derivatives of mercury can have, in principle, different and frequently unexpected structures[109], since kinetic study of their rearrangements, including C,O-transitions, is virtually impossible without a preliminary unambiguous determination of the structure of the substance.

for comparison. In the fixed isomers (XIVb), which are detected at fairly low temperatures, the degrees of shielding of the 3- and 5-CH_3 groups in the case of [M] = HgC_6H_5 differ appreciably. In contrast to organomercury derivatives, the separation of the signals due to the methyl protons is not observed in the ^1H NMR spectra of the initial pyrazoles {[M] = H} up to −110 °C.[17] This may be caused either by the higher mobility of the tautomeric system with [M] = H or by the unduly small difference between the degrees of shielding of the 3- and 5-methyl groups in the fixed tautomers. The data obtained in studies[121,122] where the splitting of the signals due to the $C_{(3)}$ and $C_{(5)}$ nuclei in compounds (XIV) with [M] = H and R = X = H, was observed in solvating solvents by $^{13}C-\{^1H\}$ NMR (at −110 °C in a mixture of diethylether and tetrahydrofuran[121] and at −17 °C in hexamethylphosphoramide[122]) apparently also support the first hypothesis.

Different mechanisms of the metallotropic transitions in the series of pyrazoles have been analysed[17]. In particular, the intermolecular N,N-transitions can occur in principle via both bimolecular and ionic mechanisms. However, the bimolecular mechanism of the formation of phenylmercury derivatives of pyrazoles tends to be disproved by the fact that the parameters of the ^1H NMR spectrum of compound (XIV, R = CH_3 and X = Cl) are independent of the concentration of this compound. Data concerning the influence of polar additives on the rate of the process may be evidence against the intermolecular transfer of the organometallic group via an ionic mechanism. It has been found that, when the polar nitromethane is added to a mixture of methylene chloride and chloroform, chosen as the main solvent, the migration of the phenylmercury group is accelerated slightly[17]. The use of a solvating agent such as pyridine as the additive also does not entail appreciable changes [which is analogous to the absence of a dependence of the rate of N,N-transitions on the solvent, observed in an NMR study of the $(CH_3)_3Si$ derivatives of pyrazole[125]].

Thus the most acceptable explanation of the ^1H NMR data obtained by Kravtsov et al.[17] is that the organomercury groups migrate between nitrogen atoms via the intramolecular 1,2-transitions (23). This mechanism presupposes the coordination of the mercury atom in its transition state to both nitrogen atoms of the heterocycle.

Solvating solvents exert different types of influence on the prototropic and metallotropic N,N-transitions in pyrazoles. Thus the addition of the polar nitromethane to a solution of compound (XIV) with [M] = H and X = Cl[116] as well as [M] = HgC_6H_5[17] has only an insignificant influence on the process. However, the addition of pyridine leads to a sharp acceleration of the prototropic process although this type of influence by pyridine has not been observed for [M] = HgC_6H_5. These findings apparently indicate a difference between the mechanisms of the N,N-transitions in the solvents employed. For cationoid species of other types, for example, [M] = SiR_3 and $Ge(CH_3)_3$, the results of studies by dynamic NMR[123-125] show that, as for [M] = HgC_6H_5, the N,N-transitions take place intramolecularly. These NMR data make it possible to set up sequences (26) and (27) based on the relative increase of the mobilities of the cationoid species in the series of pyrazoles as a function of their nature[26,27]:

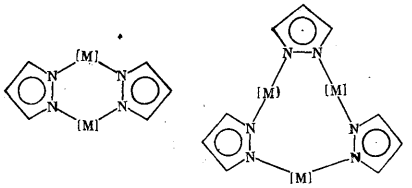
$$Si(OC_6H_5)_3 < Si(CH_3)_3 \sim Si(C_2H_5)_3 < Ge(CH_3)_3 < Sn(C_4H_{9}\text{-}n)_3 \quad (26)$$

$$SiR_3 < Ge(CH_3)_3 < HgC_6H_5 . \quad (27)$$

The available NMR data also permit certain inferences concerning the influence of substituents in the anionoid residue on the rates of the N,N-transitions. For example, an increase of the electron-donating capacity of the substituents in the 3- and 5-positions is accompanied by the acceleration of the 1,2-transitions of the organosilicon and organogermanium groups:

$$CF_3 < H < CH_3 . \quad (28)$$

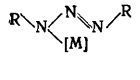
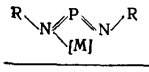
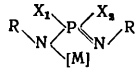
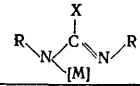
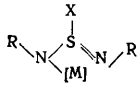
In conclusion we emphasise that the intramolecular mechanism formulated for the group of cationoid species considered, [M] = HgR, SnR_3, GeR_3, and SiR_3, for which the compounds (XIVa) are monomeric, cannot be transferred mechanically to pyrazoles with cationoid species of other types:



(XVa) (XVb)

The simplest example of explicit differences is provided by the case with [M] = H for which the trimeric structure (XVb) has been postulated[21], in the ground or transition states and for the description of the N,N-transitions of which one evidently cannot use mechanism (20). The pyrazole derivatives of univalent gold, [M] = Au, have an analogous structure in the ground state[127,128]. The dimeric structure (XVa) in the ground state has been established for yet another group of cationoid species with [M] = BR_2, AlR_2, GaR_2, or TlR_2,[129-132] and all the M–N bonds in these compounds are virtually equivalent[129].

Table 1. Certain degenerate metallotropic 1,3-transitions between nitrogen atoms in triad systems (according to NMR data).

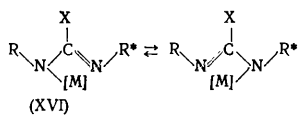
Tautomeric system	X	[M]	R	Solvent	*t*, °C*	Refs.
	—	HgC_6H_5	FC_6H_4	Py + THF + $CHCl_3$ (3:2:2)	<−120	[139]
	—	$Si(CH_3)_3$	CH_3	C_6H_6	>80	[140]
	—	$Si(OCH_3)_3$	CH_3	CH_2Cl_2	18	[141]
	—	$Si(CH_3)Cl_2$	CH_3	CH_2Cl_2	−2	[141]
	—	$Si(CH_3)_3$	$C(CH_3)_3$	C_6H_6	0	[148]
	—	$Si(CH_3)_3$	$Si(CH_3)_3$	C_6H_{12}	77	[147]
	X_1=CH_3; X_2=$C(CH_3)_3$	$Sn(CH_3)_3$	CH_3	CCl_4	<−50	[145]
	X_1=CH_3; X_2=$C(CH_3)_3$	$Si(CH_3)_3$	CH_3	CCl_4	<−50	[145]
	X_1=X_2=OCH_3	$Si(CH_3)_3$	$Si(CH_3)_3$	decalin	98	[146]
	X_1=X_2=CH_3	$Si(CH_3)_3$	$Si(CH_3)_3$	$CDCl_3$	−20	[143]
	H	$HgCH_3$	n-$CH_3OC_6H_4$	CH_2Cl_2	<−100	[142]
	H	HgC_6H_5	n-$CH_3C_6H_4$	CH_2Cl_2	<−100	[142]
	C_6H_5	$Sn(CH_3)_3$	CH_3	$CDCl_3$	<−60	[9]
	C_6H_5	$Si(CH_3)_3$	CH_3	$CDCl_3$	<−60	[9]
	CH_3	$Si(CH_3)_3$	$Si(CH_3)_3$	$(C_2H_5)_2O$	<−50	[144]

* The temperature at which the signals of the indicator nuclei merge.

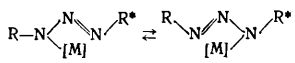
Among the odd systems, in which there is a possibility of N,N-transitions of organometallic species in principle, we shall point out, for example, the amidine triad (29) and the

diazoamine triad (30). The prototropic transformations (degenerate and non-degenerate) in the corresponding initial structures with [M] = H have so far been inadequately investigated by NMR[133-139]. There are also few data concerning the metallotropic transitions[9,139-142]. Table 1 gives a compilation of the available information about the degenerate metallotropic 1,3-transitions between nitrogen atoms in these and certain other triad systems, which have so far been established by NMR. It also includes data obtained for [M] = $Si(CH_3)_3$, because they make it possible to discover certain tendencies useful in the analysis of metallotropic transitions proper.

Degenerate metallotropic N,N-transitions of the amidine type were first observed in 1968[9] in the study of the ^1H NMR spectra of N,N-dimethylbenzamidine derivatives (XVI) with [M] = $Sn(CH_3)_3$ or $Si(CH_3)_3$, R = CH_3, and X = C_6H_5.[9]



(XVI) (29)



(30)

It has been found that the signals of the non-equivalent *N*-methyl groups observed separately at −60 °C merge into a singlet with increase of temperature, which indicates acceleration of the N,N-transitions (29). This migration apparently takes place intramolecularly, which can be inferred from the absence of a dependence of the NMR spectra on the concentrations of the compounds and also from the observation in the case of [M] = $Sn(CH_3)_3$ even under fast dynamic conditions of satellites due to the spin–spin interaction of the ^{117}Sn and ^{119}Sn nuclei with the protons of the N–CH_3 groups[9]. For [M] = H, a singlet due to the indicator protons has also been observed at room temperature.

The results of a study[142] in which an attempt was made to observe N,N-transitions (29) of organomercury groups in compounds (XVI) with [M] = HgC_6H_5 or $HgCH_3$, X = H, and R = aryl permit additional conclusions. The ^1H NMR spectra of these compounds at temperatures up to −100 °C do not exhibit a splitting of the signals due to the indicator group protons (Table 1), which can be explained either by the unduly high rate of the N,N-transitions (29) or by the symmetrical structure of the compound in which the metal atom is linked simultaneously to both nitrogen atoms. Bearing in mind that the latter hypothesis conflicts with X-ray diffraction data[142], presumably the 1,3-N,N-transitions (29) of the organomercury groups in the amidine triad are appreciably faster than the transitions of the organotin groups.

The proton N,N-transitions in the open diazoamine systems (XVII) have been investigated frequently by NMR, but the majority of these studies refer to non-degenerate transformations with [M] = H and R ≠ R*. The retardation of the proton transitions (30) in the degenerate case has been noted in only one study[138].

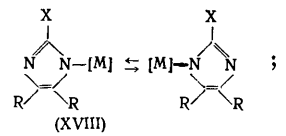
The study of degenerate metallotropic N,N-transitions (30) has begun only recently. Thus it has been observed[139] that, in contrast to di-(4-fluorophenyl)triazenes, the N,N-transitions (30) in their phenylmercury derivatives (XVII) with [M] = HgC_6H_5 and R = 4-FC_6H_5 are so fast that even in the temperature range from −90° to −120 °C only a consecutive broadening of the fluorine signal is observed, which may be evidence in support of some retardation of the intramolecular metallotropic transitions (the intermolecular migration of the phenylmercury groups takes place at higher temperatures). It is interesting to compare these results with data obtained for the N,N-transitions of organosilicon groups[140,141]. For [M] = SiR_3, the N,N-transitions (30) are also intramolecular and their rate depends significantly on the structure of the groups in [M]:

$$SiCH_3(C_2H_5)_2 < Si(CH_3)_3 < Si(CH_3)_2OCH_3 < SiCH_3(OCH_3)_2 < Si(OCH_3)_3 < \\ < Si(CH_3)_2Cl < Si(CH_3)Cl_2 < HgC_6H_5 \quad (31)$$

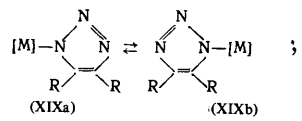
Presumably sequence (31) is associated with the increase in the same order of the coordinating capacity of the key element (Si or Hg), which facilitates the formation of the transition state.

The results of the NMR study of dynamic processes also in the series of derivatives of certain transition metals are available[149-153], but, bearing in mind the fact that the triazene ligand in transition metal complexes can behave not only (and not so much) as a monodentate species but also as a bidentate or bridging species[153-156], it is natural to suppose that the correct interpretation of these results requires the determination of independent data on the structure of the compounds, particularly on the type of bond between the organometallic group and the anionoid residue.

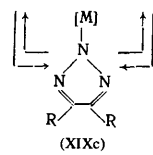
Among cyclic systems, imidazoles (XVIII) and vicinal 1,2,3-triazoles (XIX) are the simplest and most natural analogues of triads of the amidine and diazoamine types. As regards the possible metallotropic N,N-transitions, the most interesting feature of these nitrogen heterocycles is that, in contrast to the amidine and diazoamine triads (29) and (30), a planar four-unit cyclic transition state incorporating the M atom and three atoms of the triad cannot be formed in such systems:



(XVIII) (32)



(XIXa) (XIXb) (33)

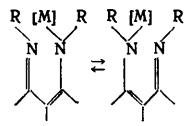


(XIXc)

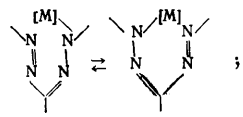
The question of the possible metallotropy in imidazoles can be considered in relation to cationoid groups such as $Si(CH_3)_3$ and $Ge(CH_3)_3$. Thus a study[157] of the ^{13}C NMR spectrum of trimethylsilyl derivatives of imidazole (X = CH_3, R = H) in the absence of a solvent demonstrated the non-equivalence of the $C_{(4)}$ and $C_{(5)}$ atoms even at room temperature. An analogous phenomenon has been observed in the study of the ^1H and ^{13}C NMR spectra of *N*-trimethylsilylimidazole and the ^{13}C NMR spectrum of an *N*-trimethylsilyl derivative of 2-methylimidazole in triethylamine. These results showed that, for [M] = $Si(CH_3)_3$, intramolecular 1,3-transitions (32) do not occur in imidazole. However, it has been established[157] that traces of water, usually present even in highly purified specimens of trimethylsilylimidazoles, catalyse intermolecular

N,N-transitions of the $(CH_3)_3Si$ groups¶. This conclusion was confirmed by the measurement of "frozen" ^1H and ^{13}C NMR spectra of trimethylsilyl derivatives of imidazoles and 2-methylimidazole in the study of each in triethylamine and by the acceleration of N,N-transitions following the addition of water. The intermolecular nature of the N,N-transitions was confirmed in the study of the ^{13}C NMR spectra of a mixture of trimethylsilyl derivatives of imidazole and 2-methylimidazole.

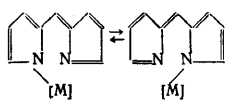
From the standpoint of metallotropic N,N-transitions, vicinal 1,2,3-triazoles (XIX) have yet another feature which distinguishes them from triazenes and is associated with the indefinite nature of the "instantaneous" structure of these compounds for different [M]. In particular, the fact that the ^{13}C NMR signals corresponding to the $C_{(4)}$ and $C_{(5)}$ nuclei are not resolved up to −50 °C for $[M]=SnR_3$[158] can be accounted for by the symmetrical structure of compound (XIXc) (all these compounds are monomeric in solution) and not by the rapid migration of the SnR_3 group between the nitrogen atoms via process (33). Although the authors themselves[158] are inclined towards the first hypothesis, the second explanation is no less ligitimate. Thus further study of the metallotropic transitions in the series of vicinal triazoles should be preceded by an unambiguous determination of their "instantaneous" structure:



(34)

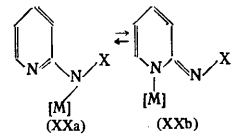


(35)



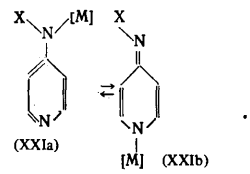
(36)

Only a few studies have been made on the question of the N,N-transitions of cationoid species in the pentads (34)–(36) and mainly for the case where [M] = H. In particular, low-temperature NMR measurements do not permit the detection of the prototropic transitions (36).[159] It has been suggested[160] on the basis of NMR data that, for $[M]=Tl(CH_3)_2$, the organometallic species is linked simultaneously to both nitrogen atoms. Although this conclusion is entirely likely, a more rigorous treatment requires the corresponding low-temperature measurements in order to throw more light on the question of the "instantaneous" structure of the compound with $[M]=Tl(CH_3)_2$: whether the metal in this derivative is tetracoordinate or tricoordinate and whether it executes rapid N,N-transitions:



(37)

An instance of non-degenerate N,N-transitions has been found[4,5] in an ultraviolet spectroscopic study of solutions of phenylmercury derivatives of 2- and 4-phenylsulphonylaminopyridines (representing respectively an aminopyridine triad and pentad). The simultaneous existence in solution in acetonitrile of the two possible tautomeric forms of these compounds—the aminopyridine form (XXa) or (XXIa) and the pyridone imine form (XXb) or (XXIb)—and their interconversion via non-degenerate metallotropic transitions of the amidine type (37) or (38) for $[M]=HgC_6H_5$ and $X=SO_2Ar$, has been demonstrated. A dependence of the tautomer ratio on the nature of the medium has been established. In particular, in dioxan equilibria (37) and (38) are almost wholly displaced towards the aminopyridine form:



(38)

The influences of various factors on the shifts of the tautomeric equilibria (37) and (38) have been compared for two different cationoid groups, namely [M] = H and HgC_6H_5.[4,5] It was found that, for [M] = H, the pyridone imine forms (XXb) and (XXIb) are more stable than for $[M]=HgC_6H_5$, particularly in solvents of low polarity. The substituents in the *para*-position of the benzene ring of the SOAr group have the same effect on the position of the tautomeric equilibrium involving both 2- or 4-arenesulphonylaminopyridines and their phenylmercury derivatives.

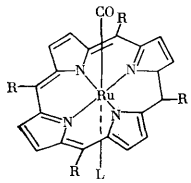
V. METALLOTROPIC N,N-TRANSITIONS IN SYSTEMS WITH M–N COORDINATE BONDS

In the tautomeric systems considered the metallotropic N,N-transitions of metal-containing species are accompanied by a rearrangement of the system of multiple bonds in the molecules. However, in principle, in organometallic derivatives one cannot rule out the possibility of the existence of tautomeric systems in which the metallotropic transition between two states does not require a redistribution of the multiple bonds. One of the types of structures of this kind can evidently consist of compounds in which [M] migrates between the heteroatoms N,O,S, etc., subject to the condition that the M–E bond is a coordinate linkage and that two or more equivalent or different atoms able to behave as donors of an unshared electron pair are available for its formation.

Such tautomeric systems have indeed been found in recent years. The first report of "non-traditional" metallotropic 1,3-transitions between nitrogen atoms appeared in 1967[161,162] and that of intramolecular 1,2-transitions was published in 1972.[163] Hitherto this phenomenon has been observed and investigated for an extremely wide variety of nitrogen-containing systems[164–183]. Several examples of degenerate

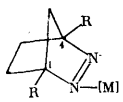
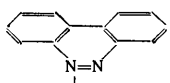
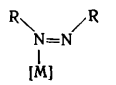
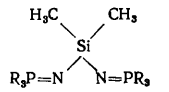
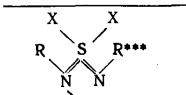
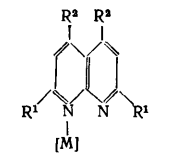
¶ In the light of these results, the results of a dynamic NMR study of imidazole derivatives, carried out for [M] = $Ge(CH_3)_3$, R = H or CH_3 and X = H by Cotton and Ciappenelli[124] and for $[M]=Si(CH_3)_3$ and R = X = H carried out by Torocheshnikov et al.,[125] apparently become more understandable. The studies were performed without taking into account the possibility of catalysis by traces of water and led the authors[124,125] to somewhat different conclusions, although they observed experimentally the same result—the identical shielding of the $H_{(4)}$ and $H_{(5)}$ nuclei as well as $C_{(4)}$ and $C_{(5)}$ nuclei over the entire temperature range accessible to investigation.

N,N-transitions of the 1,2- and 1,3-types in compounds with heterocyclic and other anionoid residues are presented in Table 2.



(XXII)

Table 2. Certain degenerate metallotropic 1,2- and 1,3-transitions between nitrogen atoms in non-traditional tautomeric systems (according to NMR data).

Tautomeric system	[M]	R	Solvent	t, °C*	Refs.
1,2-Transitions					
	$Cr(CO)_3Ar$	H	toluene-d_8	⩽50	[170]
	$Cr(CO)_5$**	—	$CDCl_3$	20	[176]
	$W(CO)_5$**	—	$CDCl_3$	20	[176]
	$Rh(CO)_2Cl$	—	$CDCl_3$	20	[178]
	$W(CO)_5$	iso-C_3H_7	$(CD_3)_2CO$	−30	[177]
1,3-Transitions					
	$Al(CH_3)_3$	CH_3	CH_2Cl_2	−60	[162]
	$Ga(CH_3)_3$	CH_3	CH_2Cl_2	−60	[162]
	$In(CH_3)_3$	CH_3	CH_2Cl_2	<−70	[162]
	$Al(CH_3)_3$	$Si(CH_3)_3$	CH_2Cl_2	−60	[166]
	$Al(CH_3)_3$	$Ge(CH_3)_3$	CH_2Cl_2	−60	[166]
	$Au(CH_3)_2X$****	R^1=CH_3, R^2=H	CH_2Cl_2	−90	[167]
	$Pt(PEt_3)Cl$	R_1 = R_2=H	$CD_2Cl_2/(CD_3)_2CO$	−70	[180]

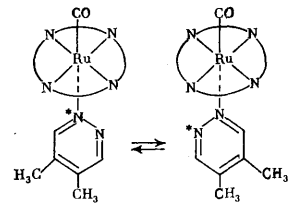
* Temperature at which the indicator nuclei are detected separately.

** ^{13}C NMR.

*** X = CH_3 or C_2H_5.

**** X = Hal, OCN, etc.

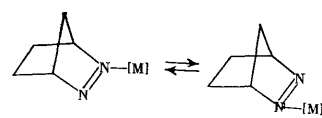
Eaton et al.[163] investigated by dynamic ^1H NMR several complexes of type (XXII), where R = iso-C_3H and L = mono- or di-nitrogen heterocyclic ligand. It was found that in the case where L = 4,5- or 3,6-dimethylpyridazine, 1,2-transitions can occur intramolecularly:



(39)

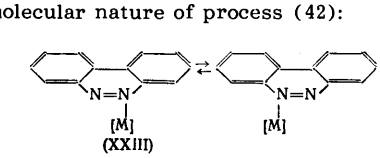
In particular, when L = 4,5-dimethylpyridazine at solution temperatures below approximately 12 °C, the signals corresponding to the indicator methyl groups are observed separately. With increase of temperature the signals broaden, approach one another, and finally merge into a single signal. The temperature dependence of the NMR line form for the complex in the presence of an excess of the free ligand permitted the conclusion that, in the range from −24° to +40 °C, process (39) is intramolecular, while at temperatures in the range 30–150 °C it also becomes intermolecular. Analogous results have been obtained in the study of the ruthenium complex of 3,6-dimethylpyridazine. In this case the process proceeds intramolecularly at lower temperatures, while above −43 °C it can also take place intermolecularly[163].

A study[170] of compounds of the type $CrAr(CO)_2L$, where L = 2,3-diazabicyclo[2,2,1]hept-2-ene, demonstrated a temperature dependence of the signal due to the 1,4-protons, which indicated the identical shielding of these protons at high temperatures and their different shielding at low temperatures. The authors suggested that these spectral changes are related to intramolecular 1,2-transitions (40) of the group [M] = $Cr(CO)_2Ar$ between the bicyclic nitrogen atoms. The study of process (40) using different aromatic ligands in [M] revealed a dependence of the free energy of activation for the process on the structure of the aromatic π-ring: $(CH_3)_6C < 1,3,5\text{-}(CH_3)_3C_6H_3 < C_6H_6 < 1,4\text{-}[CH_3OC(O)]_2.C_6H_4$.



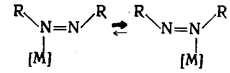
(40)

Additional information about the 1,2-transitions of groups containing transition metals has been obtained in a number of studies[176–179]. In particular, in a study of compounds (XXIII) by ^{13}C and ^1H NMR it was found that, for [M] = $Cr(CO)_5$ and $W(CO)_5$, process (41) takes place fairly rapidly at room temperature. The study of the $W(CO)_5$-complexes of the *cis*- and *trans*-isomers of 2-azopropane showed that N,N-transitions take place only in the *cis*-compounds {[M] = $W(CO)_5$, R = iso-C_3H_7; process (42)}. In this case the proximity of the neighbouring nitrogen atom reduces the activation energy for the intramolecular transition so much that the formation of a new W–N bond in the transition state requires a preliminary dissociation of the old bond. A series of pieces of evidence have been adduced in support of the intramolecular nature of process (42):

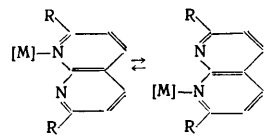


(XXIII)

(41)



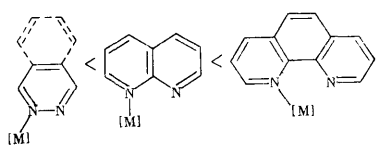
(42)



(43)

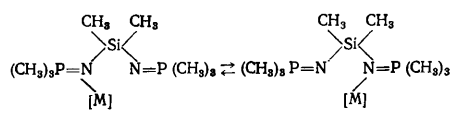
A thorough study has been made[167] of the metallotropic 1,3-N,N-transitions (43) in a series of 1,8-naphthyridine derivatives with [M] = $(CH_3)_2AuX$, X = Hal, OCN, or SeCN, and R = CH_3. At room temperature in weakly solvating solvents the ^1H NMR spectra of the compounds show that the non-equivalent methyl groups of the ligand are equally shielded, while at −90 °C their signals are converted into two separate singlets of equal intensity. The corresponding changes have been observed for aromatic protons in the 3,4- and 5,6-positions. Special experiments have established that the dynamic process is intramolecular (its characteristics are independent of the concentration of the test substance and of the addition of an excess of free 1,8-naphthyridine). This fact and also the monomeric nature of the compound permitted the conclusion that the changes in the NMR spectra are caused by metallotropic 1,3-transitions of the organogold group between the nitrogen atoms of the 1,8-naphthyridine ring. Yet another feature of process (43) should be noted: changes in the substituent X in the organogold group hardly alter the free energy of activation for the process.

Transitions of type (43) have also been studied for [M] = $MCl(PR_3)_2$, R = H, and M = Pt or Pd.[180-183] Furthermore, studies have been made of the 1,4-transitions of these metal-containing groups in a 1,10-phenanthroline complex and of the 1,2-transitions in the pyridazine and phthalazine complexes. Comparative analysis of the NMR data led to the conclusion that the rate of the N,N-transitions of the metal-containing group increases in the sequence:



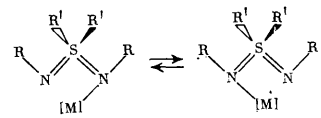
The increase takes place as the orientation of the unshared electron pair of the non-coordinated nitrogen atom becomes more favourable for the formation of a transition state in which both nitrogen atoms are linked simultaneously to the metal atom. In the palladium derivatives the rate of the process is higher than in the platinum compounds.

A comparative study has been made[161,162] of the 1,3-N,N-transitions (44) of the organometallic groups [M] = $Al(CH_3)_3$, $Ga(CH_3)_3$, and $In(CH_3)_3$:



(44)

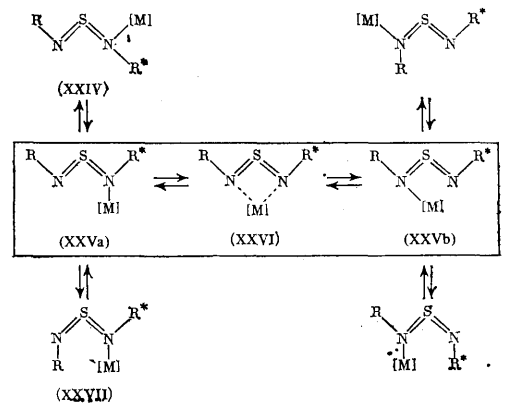
The ^1H NMR spectra of these derivatives at room temperature showed, as for the free ligand, a single doublet signal corresponding to the protons of the $(CH_3)_3P$ group. With decrease of temperature the signal broadens and in the case of the aluminium and gallium derivatives is split into two doublets of equal intensity; for the indium compound the splitting is not achieved even at −70 °C. The authors[152] concluded that they observed intramolecular 1,3-N,N-transitions (44) (their rate is independent of the addition of the non-coordinated ligand) of the groups $M(CH_3)_3$, whose rate increases in the sequence $Al(CH_3)_3 < Ga(CH_3)_3 < In(CH_3)_3$. Presumably this sequence is due to the increasing size of the vacant orbital of the metal with increase of its atomic number, which facilitates the formation of the transition state in which the metal forms a new bond before the dissociation of the old one:



(45)

Data have been published[166] on the metallotropic N,N-transitions (45) in bis-*S*-alkyl derivatives of sulphodi-imide, where [M] = $Al(CH_3)_3$, R = $(CH_3)_3Ge$ or $(CH_3)_3Si$ and R′ = CH_3 or C_2H_5. At room temperature the ^1H NMR spectra exhibited a single signal corresponding to the indicator groups R; at lower temperatures the signal is split into two components of equal intensity. The authors[166] interpreted these results from the standpoint of fairly rapid N,N-transitions (45) of the organoaluminium group in the system. As regards the mechanism of these transitions, they occur mainly intramolecularly at fairly low temperatures, while at higher temperatures they can also take place intermolecularly.

A series of studies[171-175] have been devoted to the structure of and dynamic, including metallotropic, processes in sulphodi-imide derivatives of transition metals without substituents at the sulphur atom. Sulphodi-imides non-alkylated at the sulphur atom themselves undergo intramolecular dynamic transformations in the temperature range investigated by the authors (mainly as a result of the internal rotation about the S = N bond). This complicated the interpretation of the phenomena concerning the NMR spectra of the sulphodi-imide complexes of transition metals. Furthermore, one must take into account the fact that, on formation of these complexes, the sulphodi-imides can function not only as N-donors but also as S-donors or chelates, depending on the nature of the metal-containing group:



(46)

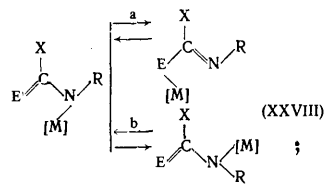
In the interpretation of the ^1H and ^{13}C NMR spectra of the sulphodi-imide derivatives of platinum(II), palladium(II), rhodium(I), and iridium(I) the authors considered several possible types of transformations, mainly intramolecular ones [the processes (XXIV) ⇌ (XXVa), (XXVII) ⇌ (XXVa), and (XXVa) ⇌ (XXVI) ⇌ (XXVb) via mechanism (46)]. Among these, only the reaction (XXVa) ⇌ (XXVb) is a metallotropic N,N-transition, which involves the intermediate formation of the transition state (XXVI) and which proved to be extremely sensitive to different structural factors. It has been found that the N,N-transitions depend appreciably on the properties of the metal and its environment and begin to be observed in the NMR spectra at temperatures from −45° to +60 °C; their rate decreases in the sequence Rh^I, Ir^I > neutral Pd^{II}, cationic Pt^{II} > neutral Pt^{II}.

A number of workers[172,174,175] were able to find several compounds in which the ligand exists mainly in the *trans, trans*-form (XXV) (and in which the dynamic processes observed by NMR can be explained exclusively by metallotropic N,N-transitions), in particular, a number of bivalent platinum complexes. A distinct separation of the signals corresponding to the indicator aryl groups is observed at −20 °C in the ^1H and ^{13}C NMR spectra of the complexes (XXV) with R = Ar and [M] = *trans*-$PtCl_2L$, while at 0 °C these signals have already merged. The N,N-transitions (46), whereby the authors[172] explained the observed spectral changes, proved to be intramolecular, because their rates were independent of either the concentration of the platinum complex or of the addition of the free ligand to the solution; however, above 30 °C the process was found to take place also via an intermolecular mechanism.

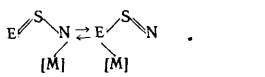
Among other features of reaction (46), the following have been noted. Firstly, it has been found that the rate of the N,N-transitions of platinum in diarylsulphodi-imides increases with decrease of the electron-donating capacity of the ligand L: $PR'_3 > AsR'_3 > SbR'_3$. Secondly, the rate of the process increases on enhancement of the electron-accepting properties of the aryl substituents and is therefore greater for R = Ar than for R = Alk. According to the authors, these results can be explained by the fact that the electron-accepting constituents are capable of stabilising the transition state (XXVI).

VI. N,E-TRANSITIONS (E = O, S, or Se)

Fairly numerous studies have been made of the dynamic transformations in the triads (47)[184-200] and (48)[201,202] (E = O or S). The interpretation of the results is in many instances difficult because of the possibility of dynamic changes of two types in these compounds—the 1,3-N,E-transition (47a) of the cationoid group and the internal rotation (47b) about the C–N bond in the amide(thioamide) form:



(XXVIII) (47)



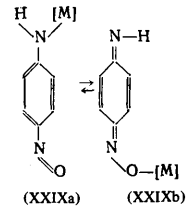
(48)

In particular, when E = O, processes (47) were investigated in relation to different cationoid species and the occurrence of the amido-amidol N,O-tautomerism was noted for [M] = $Al(CH_3)_2$,[184] BR_2,[185] and SiR_3.[175]

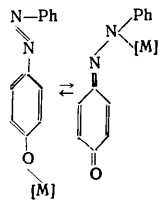
It has been shown for [M] = $Si(CH_3)_3$ and X = CH_3 that the N,O-transitions (47a) take place intramolecularly and that the *para*-substituents in R = aryl alter appreciably the ratio of the tautomers, promoting a shift of the equilibrium in the direction of the imidol form (XXVIII) in the sequence[197] $OCH_3 < CH_3 < H < Cl < NO_2$.

The 1,3-migration (47a) and the internal rotation (47b) have also been investigated for E = S, but in relation to a smaller number of examples.

A study has been made[2] of several potentially tautomeric systems in which there is a possibility of the metallotropic N,O-transitions (49) and (50)—nitrosoanilines (XXIX), hydroxyazo-compounds (XXX), and quinone phenylhydrazones:



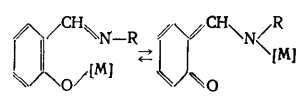
(XXIXa) (XXIXb) (49)



(XXXa) (XXXb) (50)

In the study of nitrosoanilines, nitrosonaphthylamines, and their arylmercury derivatives a similarity was observed in the behaviour of cationoid species such as [M] = H and [M] = HgC_6H_5 from the standpoint of the tautomeric equilibrium (49); both organometallic derivatives and their unsubstituted analogues have the nitrosoamine structure (XXIXa) in solution (in contrast to nitrosophenols, for which the quinonoid form predominates). However, in the sodium salts of nitrosoanilines and nitrosonaphthylamines the anions exist in the quinonoid form. Similar results have been obtained in the study of hydroxyazo-compounds and their arylmercury derivatives (XXX). For cationoid species of both types—[M] = H and [M] = HgAr—the benzenoid structure (XXXa) is typical both in solution and in the solid state.

Yet another example of metallotropic tautomeric systems is provided by the organometallic derivatives of *o*- and *p*-hydroxyarylaldimines[203]. In particular, analysis of electronic and luminescence spectroscopic data for o-compounds of type (XXXI) with [M] = $HgCH_3$, HgC_6H_5, or $Tl(C_2H_5)_2$ led to the discovery of non-degenerate O,N-transitions (51). As for [M] = H, in non-polar solvents equilibrium (51) is almost wholly displaced towards the benzenoid O-form (XXXIa), while in solvating media the content of the quinonoid tautomers (XXXIb) also becomes appreciable. A shift towards the quinonoid form is likewise observed following a decrease of temperature. It is striking that in the crystalline state compound (XXXI) with [M] = HgC_6H_5 exists entirely in the quinonoid N-form[204]. The occurrence of O,N-transitions has also been observed in the phenylmercury derivative of *p*-hydroxyarylaldimine[203]:

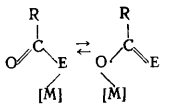


(XXXIa) (XXXIb) (51)

VII. O,E-TRANSITIONS (E = O, S, or Se)

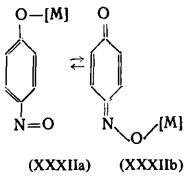
There are virtually no NMR data on degenerate metallotropic O,O-transitions in triads such as [M]–O–N=O and R–C(=O)–O–[M] and their determination will be limited by the

degree of development of the ^{17}O NMR method. It is methodologically simpler to investigate the non-degenerate tautomeric transitions (52) in triads of this kind, which can occur, for example, when $E \neq O$. Such a process has been investigated, in particular, for $E = Se$, $R = CH_3$, and $[M] = SiH_3$[205, 206]. By varying the conditions of the measurement, it was possible to observe in the ^1H NMR spectra both possible states of the system—either two sets of signals due to the SiH_3 group and the indicator group R, corresponding to slow O,Se-transitions of the SiH_3 group within the framework of non-degenerate interconversions of the O- and Se-isomers, or a single set of signals corresponding to the indistinguishability of the isomers owing to their rapid interconversion. Special experiments showed that reaction (52) is intramolecular:



(52)

An example of non-degenerate O,E-transitions can also be provided by the O,O-transitions in compounds with structurally non-equivalent oxygen atoms. Such compounds have been studied, in particular, in the investigation of Nesmeyanov and Kravtsov[1] mentioned above and in a subsequent investigation[7]. The authors studied the absorption spectra of organometallic derivatives of *p*-nitrosophenols (XXXII) with $[M] = HgC_6H_5$, $Sn(C_6H_5)_3$, or $Pb(C_6H_5)_3$. The set of infrared and ultraviolet spectroscopic data obtained showed that, in contrast to the solid state, where the organometallic derivatives of nitrosophenols have only the quinone oxime structure, in solution they exist in both forms—the quinone oxime form (XXXIIb) and the nitroso-form (XXXIIa). Thus the interconversion of the tautomeric forms of these compounds in solution takes place via the rapid non-degenerate metallotropic O,O-rearrangement (53):

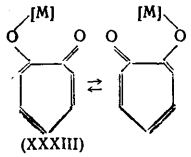


(XXXIIa) (XXXIIb)

(53)

The position of equilibrium (53) depends on a number of factors. In particular, for $[M] = Sn(C_6H_5)_3$ and $Pb(C_6H_5)_3$ in pyridine, THF, and acetone, the content of the nitroso-form is high, while in chloroform it is low. The nature of the organometallic group does not influence appreciably the position of equilibrium (53), which has been tested in relation to $[M] = HgAr$. On the other hand, the introduction of substituents into the aromatic ring of nitrosophenol lowers the content of the nitroso-form for derivatives with $[M] = Sn(C_6H_5)_3$ and $Pb(C_6H_5)_3$, as well as the initial nitrosophenols.

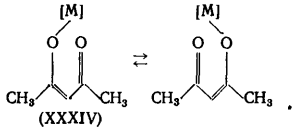
Among tetra- and penta-atomic systems, for which degenerate O,O-transitions of cationoid species have already been investigated by NMR, we shall mention the derivatives of tropolone and the enolic form of acetylacetone. However, these investigations are limited by the fact that, in relation to the majority of univalent organometallic groups, the anionoid residues of tropolone and acetylacetone behave as bidentate ligands. There are also structural difficulties associated with the inadequate knowledge about many potentially metallotropic systems. As a result, the data available at present about the O,O-dynamic processes (54) and (55) refer mainly to the case where $[M] = SiR_3$:[207-209]



(XXXIII)

(54)

Thus, in the study of compound (XXXIII) with $[M] = Si(CH_3)_2CH(CH_3)CH_2CH_3$ the $^{13}C-\{^1H\}$ NMR spectrum of the ring at 0 °C showed only four carbon signals instead of the expected seven. This result was interpreted as evidence for rapid O,O-transitions (54), which was confirmed in subsequent low-temperature measurements. Thus, for $[M] = SiR_3$ the enol–enol O,O-transitions in tropolones are comparatively rapid, in agreement with the conclusion already reached using the ^1H and ^{17}O NMR methods for $[M] = H$:[209]

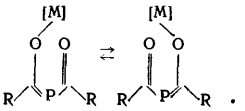


(XXXIV)

(55)

Analogous results were obtained in the study of the acetylacetonato-derivatives (XXXIV) with $[M] = Si(CH_3)_2R$[207] or $Si(CH_3)_2CH(CH_3)CH_2CH_3$.[208] Their ^1H or $^{13}C-\{^1H\}$ NMR spectra exhibit in the corresponding temperature ranges the entire set of spectral features corresponding to the dynamic process (55). The rate of transitions (55) in *cis*-acac-$Si(CH_3)_2R$ is higher than in tropolone and, depending on the nature of the group R, it increases in the sequence $CH(CH_3)CH_2CH_3 < n\text{-}C_4H_9 < C_2H_5 < CH_3 < CH_2=CH$, $C_6H_5 < CF_3CH_2CH_3$.

Certain observations have been made on the mechanism of degenerate enol–enol O,O-transitions (54) and (55) of organosilicon groups[208]. It has been found for $[M] = Si(CH_3)_2CH(CH_3)CH_2CH_3$ that both $SiCH_3$ groups give rise to separate signals in the $^{13}C-\{^1H\}$ NMR spectra in the temperature range where the occurrence of processes (54) and (55) was noted on the basis of NMR spectra. This enabled the authors[208] to conclude that the configuration at the silicon atom is preserved in the O,O-transitions of organosilicon groups and to postulate transition states for these processes. In our view, this result can also serve as evidence for the intramolecular mechanism of processes (54) and (55):



(56)

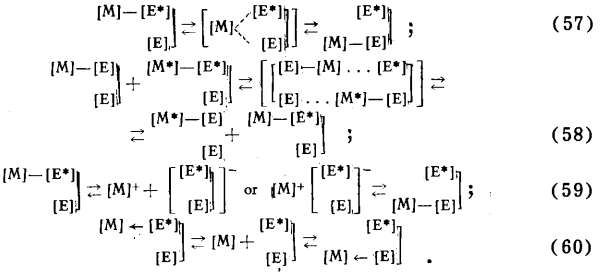
Finally, a recent communication[210] concerning the observation by NMR of O,O-transitions in a series of diacylphosphines should be mentioned {process (56), $[M] = Si(CH_3)_3$, $R = C(CH_3)_3$}.

VIII. THE MECHANISM OF METALLOTROPIC E,E-TRANSITIONS

The study of metallotropic tautomeric transformations is in essence only just beginning. It is therefore as yet difficult to expect a fairly complete understanding of the mechanism of this interesting and fairly unusual group of reactions. At present one can only attempt an initial survey of the available data, to assign them to certain most probable schemes, and to discover a series of common features of the influence of various factors on the rate of the process. Additional conclusions will evidently follow when the necessary

experimental data have been obtained. However, even the data already available on the metallotropic E,E-transitions are of theoretical value and can stimulate more far-reaching, including quantum-chemical, generalisations.

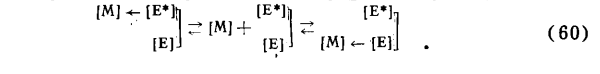
In considering the mechanism of metallotropic tautomeric transformations, one can restrict the treatment of a first approximation to four most suitable possibilities differing mainly in the characteristics of the elementary reaction steps and the form in which the cationoid and anionoid species exist:



(57)

(58)

(59)



(60)

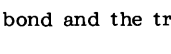
Firstly, the metallotropic E,E-transitions can take place via the intramolecular mechanism (57). This variant of the reactions is observed in many systems with cation-accepting centres in close proximity in space, particularly in different triads.

The second possibility involves the intermolecular transfer of the cationoid species [M] in the synchronous transition in the course of the interaction of two or more molecules. This mechanism [for example, mechanism (58)] does not presuppose the dissociation of the molecules into individual cationoid and anionoid residues, but after the metallotropic transition step the species[M] is bound to the residue of the partner-molecule and not to its "own" anionoid residue.

Some derivatives can dissociate into kinetically independent species. For compounds with fairly ionic [M]–[E] bonds, these are usually the ions $[M]^+$ and $[\overline{E\ E}]^-$ or their ion pairs, including solvent separated pairs. In the latter case the metallotropic transition (59) consists in the fact that the cationoid species can be linked to an anionoid residue, but this time a "foreign" one and not its "own" residue.

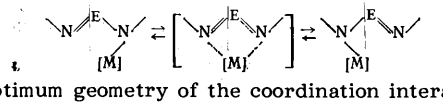
Finally the fourth possibility consists in the decomposition of the compound into neutral independent species, which are subsequently rejoined, and involves the metallotropic transition (60). This variant of the mechanism is characteristic of derivatives in which the coordinate bonds M ← E is formed between the groups [M] and $[\overline{E\ E}^*]$. In this case the anionoid and cationoid residues of the compound are stable neutral formations and can therefore exist independently in solution for a long time.

Within the framework of modern ideas[211,212], the first two mechanisms are of the associative type and the last two are of the dissociative type. We may note that the metallotropic transitions (59) are relatively atypical for the organometallic derivatives considered. On the other hand, the E,E-transitions (60) are already known in many instances (Section V). However, these data are so far insufficient for the interpretation of the characteristics of the decomposition of compounds into kinetically independent species, which is the rate-limiting stage of the metallotropic transition.

The structure of the compounds in which the intramolecular metallotropic transitions discovered hitherto take place in most cases is such that the metal atom forms a bond with one of the E atoms of the anionoid residue $[\overline{E\ E}^*]$ (E = N, O, S etc.) and is at the same time fairly close to the other E atom. Here it is envisaged that in the ground state of these compounds the distance between M and E* can be fairly large, but the relative positions of the three atoms in the given molecule—M, E, and E*—ensure the formation of a new M...E* bond and the transition state  even before the complete dissociation of the old M–E bond. In other words the elementary step of the intramolecular E,E-transition involves the virtually simultaneously dissociation of the old M–E bond and the formation of a new M–E* bond in which the potential barrier is overcome, but the system does not dissociate into kinetically independent species.

It must be emphasised that the "principle of geometrical proximity" formulated in this way, which presupposes the spatial proximity of the cation-accepting centres between which [M] migrates, constitutes a necessary but not sufficient condition for the intramolecular mechanism of metallotropic transitions. Apart from this, certain other factors, which also promote the transitions of the groups [M], are likewise important: the flexibility of the anionoid residue, facilitating the mutual approach of the cation-accepting centres, the marked electron-accepting properties of [M] and the electron-donating properties of E, and the correspondence between the geometry of the transition state and the optimum geometry of the coordination interactions for the given metal atom. However, ultimately all these factors are in some way related to the decrease of the barrier height on the potential energy curve for the E...M...E* system, which must be overcome in order to form the transition state without the dissociation of the system into kinetically independent species.

The postulate of a cyclic structure for the transition state may be adopted as one of the hypotheses concerning the elementary step in intramolecular metallotropic transitions. For example, the 1,2-transitions in pyrazoles and in general any 1,2-transitions, as well as many but by no means all 1,*n*-transitions satisfy this condition. In particular, the limitation may refer to systems of the triad type in which the atoms comprising the triad form part of the ring. This last refinement is associated with the virtual impossibility of ensuring the planarity of the transition state in small rings, as has been shown, for example, by a comparison of data for metallotropic transformations of the imidazole [reaction (32)] and amidine [reaction (29)] types. As mentioned above, in imidazoles the 1,3-transitions (32) take place only intermolecularly if at all[157], while in amidine derivatives the intramolecular process (29) takes place very readily[142], as in the case of the diazoamine triad (30). Evidently this clear difference is associated with the possibility of the formation in the latter case of a planar four-membered transition state, so that in this instance the fundamental step in the metallotropic transformation is a synchronous transformation of the bond system (E = N or CR):



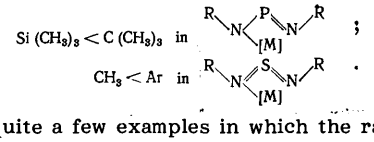
The optimum geometry of the coordination interactions for the given organometallic group may also be important[213]. Thus, the high migratory capacity of RHg groups compared with R_3Sn in intramolecular metallotropic processes can be partly attributed to the fact that a T-shaped geometry of the coordination interactions, close to the geometry of the coordination interactions in the formation of a cyclic transition state in intramolecular metallotropic processes, is optimum for the compounds RHgX,[214] while for the compounds R_3SnX the optimum geometry of coordination interactions is trigonal bipyramidal[215], in which the additional ligand occupies an axial position and which does not correspond to the coordination geometry of a cyclic transition state.

It must be emphasised that it is useful to consider metallotropic E,E-transitions only in structures where a mesomeric structure with delocalised bonds is not formed for geometrical or other reasons, as a result of which the potential of the E...M...E* system requires a single-well configuration in the structures considered, of the kind observed, for example, in dimeric derivatives of pyrazole $\{[M]-L\}_2$ with $[M]=TlR_2$, etc., and not a two-well configuration.

We shall consider in relation to known examples certain factors tending to accelerate the intramolecular metallotropic transitions.

In many instances the important factor determining the rate of E,E-transitions is the lability of the dissociating M–E bond, which increases with increase of its polarity and depends in its turn on the difference between the electronegativities of the atoms E and M and on the polar effects of the substituents. This is indicated, in particular, by the series characterising the influence of substituents attached directly to the metal in the cationoid species [M] on the rate of 1,2-transitions in pyrazoles and indenes (see Sections II and IV); $OCH_3 < Cl < C_6H_5 < CH_3$. In this case the σ-electron-accepting substituents, which reduce the polarity of the M–E bond, lower the capacity of the group [M] for migration, while electron-donating substituents increase it.

An analogous conclusion can apparently be reached by considering the influence of the substituents in the anionoid residue attached directly to the atom E. In contrast to the previous case, in the anionoid residue the polarity of the M–E bond decreases under the influence of electron-donating and not electron-accepting substituents. This influence of the substituents R has in fact been found experimentally[147, 148,171,172] for certain 1,3-transitions:



There are quite a few examples in which the rate of metallotropic E,E-transitions depends greatly on the ease of formation of the new bond. In this case the Lewis acidity of the metal in the cationoid species [M] and the basicity of the second cation-accepting centre can be regarded as the driving forces of the metallotropic tautomeric transformations. Indeed, data for the metallotropic C,C- and N,N-transitions in many organometallic systems have shown that the mobilities of different groups [M] in the E,E-transitions under consideration give rise to the following sequence: $R < SiR_3 < GeR_3 < SnR_3 < HgR$. Bearing in mind that the Lewis acidity of the metal atom in [M] increases in the same sequence, presumably the enhancement of the acidity of the metal tends to decrease the height of the potential barrier in the formation of the transition state and hence to facilitate the metallotropic transitions. An analogous conclusion follows from data for the influence of substituents in the cationoid residues of tautomeric systems such as triazenes and acetylacetonates[207,208]. In this case the substituent series, $C_4H_9 < C_2H_5 < CH_3 < OCH_3 < Cl$, is the opposite to that found for pyrazoles and indenes. An evident cause of this difference may be the difference between the geometries of these two groups of compounds. Whereas in the case of pyrazoles and indenes, which have a rigid geometry, the polarity of the dissociating M–E bond is more important, in compounds with a more flexible structure, such as, for example, triazenes and acetylacetonates, the rate of the process depends to a great extent on the ease of formation of the new M–E* bond. As a result, the enhancement of the electron-accepting properties of the substituents in [M], which renders the atom M more acid, is accompanied by the acceleration of the metallotropic transitions and not their retardation. It is natural to suppose that in this instance the substituent effects refer not so much to the M–E bonds as to a change in the acidity of the atom M, which facilitates or hinders the formation of the new M–E* bond.

Data concerning the ratio of the rates of the E,E-transitions of cationoid species such as $[M]\neq H$ and $[M]=H$ in related systems show that, whereas intramolecular tautomeric transformations are more characteristic of metallotropic transitions, intermolecular transformations of the synchronous type—bimolecular and in general n-molecular—are encountered much more frequently than in prototropic systems. In particular, O,O-transitions in acetylacetonate and tropolone derivatives with $[M]=H$ take place much faster than for $[M]=SiR_3$[207–209] {we may note that the C,C-transitions, which proceed via an intramolecular mechanism for both $[M]\neq H$ and $[M]=H$, are faster than the proton transitions for $[M]=HgR$, SnR_3, GeR_3, SiR_3, etc.}.

This may be caused also by the different capacities of the compounds considered for dimer formation and by their structural differences in the dimeric state. Many experimental data have shown that prototropic systems with bidentate anionoid residues form fairly frequently, if only for a short time, dimeric structures with non-equivalent bonds[216–218]:

$$\begin{bmatrix}[E]-H\ldots[E]\\ [E^*]\ldots H-[E^*]\end{bmatrix}\quad\begin{bmatrix}[E]\ldots H-[E]\\ [E^*]-H\ldots[E^*]\end{bmatrix}$$

These apparently include also tropolone and acetylacetonate derivatives, since prototropic transitions in these systems can proceed via an intermolecular mechanism, within the framework of the hydrogen bonds arising on formation of the dimer, and not via an intramolecular mechanism {as for $[M]=SiR_3$}. A similar explanation can be put forward in the interpretation of the results of the study of N,N-transitions in diaryltriazenes.

It is noteworthy that the capacity for the formation of associated species is characteristic also of the derivatives of certain metals among those considered here, in particular, tin, cadmium, and thallium, but in many instances, for example for $[M]=Tl$, the bonds are equivalent in the dimerisation process by virtue of geometrical and other causes, as a result of which the potential surface for the [E]–[M]–[E*] fragment is a single well:

$$\begin{bmatrix}[E]-[M]-[E^*]\\ [E^*]-[M]-[E]\end{bmatrix}$$

and the metallotropic transition considered here correspondingly loses its significance.

Certain preliminary considerations concerning the possible nature of the influence of the solvent on the rates of metallotropic processes can also be formulated. Thus it is to be expected that polar but weakly coordinating solvents will facilitate intramolecular and intermolecular metallotropic processes as a result of the polarisation, ionisation, or dissociation of the M–E bonds. Weakly polar coordinating solvents, which do not induce the ionisation or dissociation of the M–E bonds, should hinder intramolecular metallotropic processes and processes proceeding via a bimolecular mechanism by blocking the vacant orbitals of the metal atom. Finally, solvents exhibiting both a high coordinating capacity and a high polarity and capable of inducing the dissociation of the M–E bonds[219–221] should accelerate metallotropic processes, facilitating their occurrence via the intermolecular dissociative mechanism.

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The Applications of Quantum-chemical Methods to Spectroscopic Studies on Organic Compounds

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The ways of using quantum-chemical methods in the spectro-chemistry of organic compounds are considered and the advances in the calculation of electronic and vibrational spectra are characterised. The effectiveness of the combined application of quantum-chemical and spectroscopic methods and the possibility of using LCAO-MO methods for the interpretation of ultraviolet, infrared, and Raman spectroscopic data in the study of molecular structure in the ground and excited states are demonstrated in relation to a number of examples.
The bibliography includes 134 references.

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I. INTRODUCTION

A fairly complete utilisation of the potential of molecular spectroscopy, including infrared, ultraviolet, and Raman spectroscopy, can be achieved if it is possible to establish the origin of the spectral lines (bands). Useful information about the line assignments and molecular structure can be obtained from purely empirical correlations. Different variants of the additive scheme involve wider possibilities; they relate the spectra of complex molecules to the conventional parameters attributed to individual fragments, for example, chemical bonds (force constants, "electro-optical constants" of the bonds, etc.). However, in the most interesting cases—when there is a significant interaction between the fragments of the molecule—the additive scheme is greatly complicated and the possibility of an unambiguous, non-empirical, determination of the bond parameters and their physical significance are lost.

The application of quantum-chemical methods, which are based in some way on the ideas concerning the interaction of nuclei and electrons, made it possible to proceed to better-founded calculations of line frequencies and intensities with

a considerable limitation of empirical elements. Thus it has been possible to achieve a more complete and a better-founded interpretation of the spectra and to explain on this basis the characteristic features of a series of chemical and physical properties of many compounds, to obtain additional data for the description of molecular-optical phenomena, and to make semiquantitative predictions of the spectra and of the behaviour of systems which are not readily susceptible to experiments (for example, unstable intermediates).

In view of the multiplicity and non-equivalence of the quantum-chemical methods, it is useful to characterise the specific possibilities of each, to note their advantages and disadvantages, and to assess the prospects for the development of their application in molecular spectroscopy.

II. QUANTUM-CHEMICAL METHODS FOR THE CALCULATION OF SPECTROSCOPIC PARAMETERS

In the calculations of the parameters of electronic and vibrational spectra the Hartree–Fock approximation is usually employed[1]. The many-electron wave function of the molecule is found in the form of the antisymmetrical product of the one-electron wave functions—molecular orbitals (MO) $\phi_m(\mu)$—multiplied by the spin wave functions α or β of the corresponding electron:

$$\Phi_0 = \mathscr{A}\det|\varphi_1(1)\alpha(1)\varphi_1(1')\beta(1')\ldots\varphi_n(n')\beta(n')|, \qquad (1)$$

where $2n$ is the number of electrons and μ the ordinal number of the given electron. The coefficient $\mathscr{A}$ is determined by the condition governing the normalisation of $|\Phi_0|^2$ to unity.

The molecular orbitals are sought in the form of linear combinations of atomic orbitals (LCAO)

$$\varphi_m(\mu) = \sum_i C_{mi}\chi_i(\mu), \qquad (2)$$

where the C_{mi} are the required coefficients; thus the set of atomic orbitals $\chi_i(\mu)$ constitutes the basis set for the construction of the wave function ϕ_m. The principal requirement which must be met by the basis set of atomic orbitals consists in the fact that it must represent with adequate accuracy the distribution of electron density in the molecule, i.e. the basis set must be sufficiently complete. Unfortunately it is very difficult to satisfy this condition in practice. The atomic orbitals constitute an approximate representation of the electron density in isolated atoms, but their use in calculations of the electronic wave functions of molecules leads to additional errors associated with the impossibility of reproducing certain features of the changes in electron distribution on formation of valence bonds. It is therefore necessary to expand the basis sets χ_i by including additional functions in them.

The coefficients C_{mi} in Eqn.(2) are determined by a variational procedure with minimisation of the total electronic energy of the molecule E. Roothaan[2] showed that the coefficients C_{mi} corresponding to the minimum value of E can be determined from the following equations:

$$\sum_j (F_{ij} - \varepsilon_m S_{ij})\, C_{mj} = 0, \quad \sum_{ij} C_{mi}C_{mj}S_{ij} = 1, \qquad (3)$$

where

$$F_{ij} = H_{ij} + \sum_{kl} P_{kl}\left(\langle ij|kl\rangle - \frac{1}{2}\langle ik|jl\rangle\right). \qquad (4)$$

Here the summation was carried out over all the atomic orbitals k and l in the basis set. S_{ij} is the overlap integral of the atomic orbitals i and j, ε_m the energy of the electron in the mth molecular orbital, H_{ij} the one-electron Hamiltonian, P_{kl} the matrix of the bond charges and orders, and $\langle ij/kl\rangle$ the matrix element of the Coulombic interaction of electrons in the atomic orbitals χ_i, χ_j, χ_k, and χ_l:

$$\langle ij|kl\rangle = \iint \chi_i(\mu)\chi_j(\mu)\, R_{\mu\varkappa}^{-1}\, \chi_k(\varkappa)\chi_l(\varkappa)\, d\tau_\mu d\tau_\varkappa.$$

In this expression the integration is carried out with respect to the entire space of the Cartesian coordinates and $R_{\mu\kappa}$ is the distance between the electrons μ and κ.

The self-consistent field (SCF) method is used to solve the non-linear system of Eqns.(3) and (4). The set of coefficients C_{mi}, the choice of which can be fairly arbitrary, is then used as the zeroth approximation; in semiempirical methods C_{mi} are usually calculated by a procedure similar to the extended Hückel method. The matrix F_{ij} is constructed from the zeroth-approximation coefficients determined in this way and is then used, on solving Eqn.(3), to find a new set of the C_{mi}, from which a new matrix F_{ij} is constructed, etc., until the matrix elements F_{ij} and the coefficients C_{mi} cease to vary.

In practice both semiempirical and non-empirical calculations by the LCAO-MO SCF method are used.

Among the *semiempirical* procedures, the CNDO (complete neglect of differential overlap of atomic orbitals) and INDO (incomplete neglect of differential overlap) methods are commonest[3–7]. In these methods, the wave functions are calculated only for the valence electrons and the inner shells are included in the molecular skeleton; a minimal Slater basis set is used and a part of the Coulombic interaction between the electrons is neglected. In the CNDO approximation account is taken of one- and two-centre matrix elements of the Coulombic interaction of electrons only of the type $\langle ii/kk\rangle$, while in the INDO approximation the one-centre matrix elements $\langle ij/kl\rangle$, in which the i, j, k, and l orbitals belong to a single atom, are also introduced. In order to calculate all the one-centre matrix elements, the atomic spectra are used, while the two-centre integrals are evaluated from empirical formulae reflecting the dependence of the interaction between the electrons and nuclei on the relative positions of the atomic orbitals. In the second case the parameters in the empirical formulae indicated must be determined from data not only for atoms but also for small molecules; the solution of the problem is then not unambiguous and the differences between the selection procedures are characterised by modifications of the CNDO and INDO methods. A rational selection of parameters makes it possible to diminish the disadvantages of the CNDO and INDO approximations and also of the SCF method.

The CNDO/2,[5,6] INDO[7], MINDO/2,[8,9] and MINDO/3 [10] (modified INDO approximations) are most widely used to calculate the properties of the ground states of organic molecules, while electronic absorption spectra are calculated by the CNDO/S method[11,12]. A further improvement of the semiempirical methods can be achieved in terms of the more rigorous null diatomic differential overlap (NDDO) approximation.

As regards *non-empirical* calculations, here all the matrix elements of the interaction between the electrons and nuclei are evaluated by the analytical calculations of the necessary integrals in terms of a basis set of atomic orbitals. The atomic orbitals are usually Gaussian functions, which ensure a relative simplicity of the calculations but lead to a fairly poor representation of the distribution of electron density, so that one has to use many more functions than for Slater basis sets. The OST-3GF basis set—the minimal basis set of Slater orbitals each of which can be fitted by a linear combination of three Gaussian functions, is very widely

used. In the OST-4-31GF basis set, each Slater orbital for the electrons in the inner shell is described by a linear combination of four Gaussian functions and that for valence electrons is described by a combination of three and one Gaussian functions. The use of two (instead of one) linear combinations, whose coefficients in Eqn.(2) are varied independently, makes it possible to take into account the changes in the atomic orbitals on formation of different valence bonds.

The results of the calculations depend greatly on the choice of the basis set. Generally speaking, it is desirable to expand the basis set until the attainment of the Hartree–Fock limit, whereupon its further expansion no longer alters the result. However, this can be done only for the simplest molecules, for example, for CH_4 and NH_3. For more complex molecules, it is necessary to restrict the treatment to small basis sets, but their selection introduces a considerable arbitrary element into the calculation; the treatment is not universal and different basis sets must be used for different properties of the molecule. We may also note that the employment of the Hartree–Fock approximation (the SCF method) can also introduce a large error and further refinement of the electronic wave function (allowance for electron correlation) constitutes a very complex problem.

The methods described above are most widely used in quantum-chemical calculations of molecular spectra. However, their application to complex molecules is hindered by the large amount of computer time required. At the present time calculations by non-empirical methods are in practice possible for molecules consisting of not more than 6–10 atoms (20–30 electrons); semiempirical methods of the CNDO or INDO type are applicable to molecules consisting of several tens of atoms (up to 50–100 electrons). The amount of computation for more complex objects is too great even for the most efficient computers. In recent years attempts have therefore been made again to employ combined methods based on the π-electron approximation[13]. In order to take into account σ-electrons, a special empirical quadratic function was introduced, being added to the π-electronic energy of the molecule. This function contains parameters similar to the equilibrium geometrical parameters and force constants; the parameters were chosen so that the molecular geometry can be calculated by minimising the expression for the total energy of the molecule and the force constants can be calculated by differentiating the energy with respect to the atomic coordinates. Although the scope of such calculations is in many respects limited, they make it possible to investigate the spectroscopic characteristics of very large molecules.

Calculations by non-empirical methods on molecules with heavy atoms require a very large amount of computer time. The latter can be reduced by resorting to the pseudopotential method. In this approximate method one calculates the wave functions of the outer electrons only, assuming that the latter exist in the resultant electric field of the charges of the nuclei and inner electrons; the field is introduced into the Hamiltonian in the form of an empirical potential function—the pseudopotential. Calculations by this method (see, for example, Sachs and Hinze[14] and Abarenkov[15]) are much less accurate than the usual non-empirical calculations, but a successful selection of the empirical function can lead to a significant improvement of the results.

Relativistic effects, associated primarily with the high velocity of the electrons of the inner shells (involving an increase in the mass of the electron and a lag in the Coulombic potential) and with the spin–orbital interaction, play an appreciable role in the properties of molecules with heavy atoms; the shielding of the nuclear charges by inner electrons is then altered, which influences indirectly the valence electrons. Allowance for the relativistic effects increases the amount of calculation severalfold. The relevant methods for semiempirical and non-empirical calculations in LCAO-MO SCF schemes have been described in detail in a review[16].

The SCF Xα scattered wave method, the principle of which differs fundamentally from that of the widely used LCAO-MO SCF method, has been applied in recent years to the calculation of electronic absorption spectra. In the Xα method each atom is assumed to be surrounded by a sphere (different variants either do or do not allow for the overlap of the spheres of adjacant atoms); in the space between the spheres the electronic wave function is specified by planar waves and within the spheres it is sought by solving the Schrödinger equation with an empirical potential (for further details, see the relevant review[17]). The method is usually classified as non-empirical, although the specification of the potential within the spheres surrounding the atoms is partly empirical.

The Xα method makes it possible to carry out faster calculations than by the non-empirical LCAO-MO SCF methods. It is particularly effective in the study of molecules with heavy atoms containing a large number of electrons in the inner shells, since the computation time depends in this instance only slightly on the number of electrons in the atom. However, the region of applicability of this method in spectroscopy is at present largely limited to the determination of the positions of the occupied electronic levels (which are particularly important for photoelectron and X-ray electronic spectroscopy); the electronic absorption spectra are calculated much more rarely (resorting to the extremely artificial "transition state" procedure) and only the energies of transitions averaged with respect to the multiplet (!), intermediate between singlet and triplet transitions, are usually calculated, although in principle the possibility of allowing for the multiplicity is not ruled out.

III. THE FORCE CONSTANTS OF CHEMICAL BONDS AND INTRAMOLECULAR VIBRATION FREQUENCIES

The force constant of a chemical bond $K(i)$, equal to the second derivative of the potential energy of the molecule with respect to the increase in the length of the given bond: $(\partial^2 V/\partial q_1^2)_{q_j=\text{const.}}$, is perhaps the main characteristic of the mechanical properties of the bond. For like bonds in different molecules of a similar type, it varies within narrow limits; its semiquantitative correlations with the bond length and order and also certain relations with the dissociation energy are known. However, one should note that the usual force constants depend to some extent on the arbitrary element in the selection of the internal coordinate system in the molecule; the "independent force constants" d^2V/dq_1^2, which characterise the bond strength under the conditions where an external force is applied to only one (*i*th bond), are free from this disadvantage[18]. It is even more significant that the chemical bond in a polyatomic molecule cannot be, strictly speaking, characterised by a single force coefficient. For this purpose, one must introduce a whole matrix of coefficients including those related to the interaction of the given bond with all other bonds, i.e. with non-diagonal elements $K(ij) = \partial^2 V/\partial q_i \partial q_j$.[19,20] The latter determine the appearance of forces acting in the *j*th bonds as a result of the extension of the *i*th bond. The non-diagonal elements are as a rule small, but they are of primary importance for certain problems.

If the structural formula of the compound is known and the necessary set of force constants is available, it is possible to calculate fairly simply, for the conformation investigated, the frequencies ω of all the normal atomic vibrations manifested in the infrared and Raman spectra as well as vibronic absorption and secondary emission spectra, to determine the vibrational modes, and to characterise the force field in a molecule deformed in any way. These possibilities are limited in practice by the inadequacy of the information about the force constants themselves (which is particularly restricted for electronically excited states).

The total amount of information required for an exact calculation of the frequencies ω in complex molecules is extremely large and the available data must be supplemented using analogies and approximate assumptions. Under these conditions, the invocation of additional sources of information appears very important; quantum chemistry occupies a special place here, since it not only makes it possible to estimate, in principle, any force constants for both the ground and electronically excited states but it can also elucidate the origin of individual coefficients and their relation to the structure of the electron shell (unfortunately, sufficient attention has not been paid to this factor hitherto).

It is known that the solution of the converse problem—the calculation of the force coefficients from experimental frequencies ω—requires extensive and laborious preparatory work involving the synthesis of isotopic models. In many cases the solution is not unambiguous and the choice between sets of coefficients satisfying the initial system of equations is frequently based on intuition. The application of MO methods places at the disposal of the investigator independent criteria for such a choice. One can add to this that the quantum-chemical calculation of "independent force constants" does not involve any additional difficulties.

Both semiempirical and non-empirical quantum-chemical methods are used to calculate the force constants. In all cases the molecular geometry is optimised initially, i.e. the most stable form corresponding to the total energy minimum is specified; the second derivatives of the energy with respect to the Cartesian or natural coordinates (force constants) and if necessary also cubic and biquadratic terms are then found at the minimum.

The choice of the basis set has a significant influence on the results of non-empirical calculations of force constants (particularly, non-diagonal elements). Thus, when a minimal Slater basis set is used, an extremely indirect agreement with experiment is obtained. The agreement improves significantly on passing to an extended basis set (OST-4-31G, etc.), but a further extension of the latter is no longer very effective—even when the Hartree–Fock limit is reached the force constant prove to be too high by 10–20%.[21] The accuracy of the calculation of the non-diagonal elements is then much lower. Thus K(C–O, C–O′) for the CO_2 molecule was found to be too high almost by a factor of two[22]. Allowance for electron correlation improves the results[23,24], but this is virtually impossible for polyatomic molecules.

A characteristic feature of the semiempirical methods is that the deformation vibration frequencies are lower than the stretching vibration frequencies. In the CNDO/2 method the values of ω for deformation vibrations agree with experiment without the introduction of corrections, while the data for stretching modes are found to be too high. On the other hand, in the MINDO/2 method the latter are close to the experimental data, but the deformation vibration frequencies are too low. The MINDO/3 method yields results of an intermediate type; the errors are on average the same as in non-empirical calculations without allowance for electron correlation.

Since the errors are in most cases systematic, they can be greatly reduced by introducing empirically selected correcting scale factors for the determination of the types of force constant (for example, for the C–C bonds, C–C–H angles, etc.) or increments which are added to the calculated frequencies.

For calculations in terms of the MINDO/3 approximation, Dewar and Ford[25] selected a system of increments specific to stretching, deformation, and torsional vibrations of specific atomic groups or bonds; the satisfactory accuracy of the results was demonstrated in relation to a large number of examples, but the wide variety of the normal vibrational modes, which in a complex molecule include the vibrations of many bonds and angles, and the impossibility of a clear-cut separation of stretching and deformation modes limit the prospects for correcting frequencies in terms of the types of vibrations.

It appears more logical to correct the force constants and positive results have been achieved on these lines. In a non-empirical calculation of the vibrational spectra of ethylene in terms of the OST-4-31G basis set the introduction of four correcting factors (of the order of 0.75...1.0) for the diagonal force constants and of yet another correcting factor for all the non-diagonal force constants diminished the average discrepancy with 12 experimental frequencies severalfold and the latter amounted to ~7 cm^{-1}.[26] Similar results were obtained also for ethane, propane, propene, and dimethyl ether, but the corrections were chosen individually for each type of compound[27,28]. We may note that a simple determination of the frequencies from the set of coefficients $K(ij)$ obtained experimentally for other molecules of a similar type yields approximately the same accuracy in the absence of conjugation.

In the calculation of the spectra of hydrocarbons by the CNDO/2 method the following correcting factors must be introduced for the force constants[29]: 0.38 for valence bonds, 1.80 for angles in the molecular plane, and 0.62 for angles of displacement from the plane. The same corrections have been used for glyoxal and acroleine[30]. A set of scale factors for organic compounds containing N and O atoms has been recommended and tested[31]; the standard error in a series of fairly complex triazoles did not then exceed 30 cm^{-1}. We recall that the experimental error is ~±1 cm^{-1}, but the effect of the medium (solvent), which is difficult to eliminate, is an order of magnitude greater.

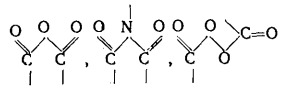
In selecting the scale factors or increments, the problem of their reproducibility in a series of different molecules naturally arises. It can be shown that it is similar to the problem of the possibility of transferring an experimental force constant, but in reality the causes of the limited universality in these two instances are completely different; in the first case such limitation arises from the significant irregularity of the errors of the selected computational method, while in the second the force field for particular test molecules has real specific features which are in themselves of extremely great interest and important for chemistry and are in addition susceptible to investigation by quantum-chemical methods.

The wide variety of procedures and correction factors reflects the subjective approach of different workers to this problem. The best results are obtained when the corrections are made specific to the maximum extent, although this inevitably reduces (and in the limit completely vitiates) the significance of the initial calculation itself.

As regards the calculations of *non-diagonal* force coefficients $K(ij)$, the latter are frequently subject to large errors and for polyatomic molecules the estimation of the accuracy of the calculations by comparison with values evaluated from experimental data is very difficult owing

to the unreliability of the latter. Practical experience with calculations has shown that semiempirical methods lead to incorrect signs of the non-diagonal coefficients characterising the interaction of the C–H bonds with adjacant valence bonds; the absolute values of these constants are low and they therefore have little effect on the frequencies, but the relative positions of the stretching vibration lines for the CH_2 and CH_3 groups depend on them. In other cases qualitatively satisfactory results were obtained. However, the non-diagonal elements were corrected by extremely arbitrary (relatively unjustified) procedures[26–31]; the correction factors were varied in the range from 0.3 to 1 (depending on the investigator who carried out the calculation and on the method used).

For non-adjacent bonds, the coefficients $K(ij)$ are extremely small and in the calculation of the frequencies ω they are therefore usually disregarded; however, in certain molecules in the presence of conjugation they proved to be fairly large, contrary to expectation. In the systems



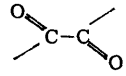
they are to a large extent responsible for the anomalously large splitting of $\omega_{C=O}$ into components corresponding to the in-phase and out-of-phase vibrations of the C=O groups[19,32]; the splitting (up to 70 cm^{-1}) and the values of $K(C=O, C=O')$ proved in this instance to be several times greater than for the system  [32,33] although seemingly the opposite should have been expected.

Table 1. The force field in terms of the symmetry coordinates for the ethane molecule (K, δ, and ρ are the stretching, deformation, and torsional force constants; subscripts S and d denote the values for symmetrical degenerate vibrations).

Force constants*	Semiempirical methods		Non-empirical methods			Experiment
	CNDO/2 (Ref.29)	MINDO/2 (Ref.29)	OST-3GF (Ref.27)	OST-4-31GF (Ref.27)	large basis set (Ref.27)	
K (CC)	4.67	5.10	6.66	4.86	5.07	4.45
K_s (CH)	5.27	5.91	7.09	5.54	5.68	4.90
K_d (CH)	5.05	5.47	7.03	5.37	5.54	4.76
δ_s	0.81	0.52	0.83	0.71	0.76	0.61
δ_d	0.77	0.37	0.89	0.72	0.69	0.56
ρ	0.81	0.53	0.94	0.82	0.85	0.68
K/K_s	0.21	0.44	−0.01	0.14	0.14	0**
K/δ_s	0.28	0.36	0.34	0.39	0.39	0.35
K_s/δ_s	−0.14	−0.09	−0.11	−0.16	−0.12	−0.05

*Units—mdyn $Å^{-1}$.

**Adopted on the basis of the assumption made.

Calculation of the principal non-diagonal coefficients for acetic anhydride by the CNDO/2 method[34] confirmed the ideas concerning the interaction of two C=O groups in the vibrational process, as a result of which $K(C=O, C=O')$ for the anhydride is much greater than for a similar molecule with a methylene bridge (pentane-2,4-dione); however, calculation revealed a feature which could not be established from experimental data, namely the significance and large contribution to the splitting of $\omega_{C=O}$ by the coefficients $K(C=O, C-O)$, which are much greater than $K(C=O, C-C)$ for pentanedione.

Certain ideas concerning the accuracy of the results obtained by different computational methods and also the coefficients $K(i)$ and $K(ij)$ themselves are provided by Tables 1 and 2, which include also fairly reliable data determined from observed frequencies; the computational methods used yielded approximately equivalent results.

It follows both from the calculation and experiment (Table 2) that the non-diagonal coefficients $K(ij)$ for a molecule with conjugated NC–CN bonds are much greater than in saturated hydrocarbons. The negative sign of $K(C\equiv N, C\equiv N')$ means that the extension of one C≡N bond favours an increase in the length of another. The diagonal coefficient $K(C\equiv N)$ is in this case lower (as for the H_2N–CN and $H_2C=CH$–CN molecules[35]) than for acetonitrile by ~3% due to conjugation, while $K(C-C)$ is in fact appreciably higher.

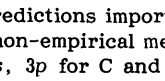
Table 2. The force constants (mdyn $Å^{-1}$) of dicyanogen and acetonitrile[35,126,127].

Force constant	Acetonitrile (experiment)	Dicyanogen				
		experimental data	INDO	MINDO/2	NMMB*	NMLB**
K (CN)	18.6	18.0	39	18	20.6	22.8
K (CC)	5.6	7.0	17.5	7.7	—	—
K (CN, C'N')	—	−0.26	−0.44	0	−0.24	−0.30
K (CN, CC)	0.15	0.42	1.8	0.7	0.14	0.09

*Calculation by a non-empirical method in terms of a moderate basis set.

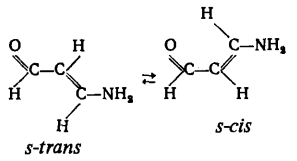
**Calculation by a non-empirical method in terms of a large basis set.

In individual studies attempts were made to investigate the accompanying molecular forms which cannot be isolated from the equilibrium system. In the communication quoted above[30] interesting data are presented for the semiempirical calculation of the spectra of the *s-cis*-conformers of butadiene and glyoxal, for which limited and unreliable information was available. According to the results[30,33], the force constants of the double bonds in the *s-cis*- and *s-trans*-conformers are virtually the same, but $K(C-C)$ for *cis*-glyoxal is appreciably smaller than for the *trans*-isomer, as a result of which ω_{C-C} is lower by 100–200 cm^{-1}. The interaction coefficients of the double bonds are in all cases small, but the symmetric vibration frequency of the double bonds in the *s-cis*-form (in contrast to the *s-trans*-form) should be lower than the antisymmetric frequency.

Detailed information has been obtained for the rotational isomers of formic acid[33]. The spectrum of the *s-cis*-conformer  was unknown and the calculation yielded predictions important for experiment. The application of a non-empirical method with a fairly large basis set (9*s*, 5*p*/5*s*, 3*p* for C and O) yielded the following force constants for the *s-cis*-conformer (*s-trans*-conformer): $K(C=O) = 14.6$ (14.1) mdyn $Å^{-1}$; $K(C-O) = 6.9$ (7.2) mdyn $Å^{-1}$; $K(O-H) = 8.8$ (7.9) mdyn $Å^{-1}$; $K(C=O, C-O) =$ 1.9 (1.3) mdyn $Å^{-1}$. In conformity with the differences between bond strengths in the *s-cis*-form, $\omega_{C=O}$ should be higher by 50 cm^{-1} and ω_{O-H} should be higher by 200 cm^{-1}. The data obtained make it possible to estimate the zero-point vibration energy and to revise the calculations of the

heats of chemical reations; on the other hand they enable one to supplement the available information about the interrelations between the $K(i)$ and the chemical bond lengths.

In the infrared spectra of certain aminocarbonyl compounds with conjugated C=C and C=O bonds, a third band, whose origin is obscure, appears in the region of 1610 cm^{-1} in addition to the bands at ~1650 cm^{-1} ($\omega_{C=O}$) and ~1570 cm^{-1} ($\omega_{C=C}$) usually observed. Calculations of the spectrum of animopropenyl[36] showed that the band is associated with the second rotational isomer and at the same time that $K(C=O)$ increases in *cis–trans*-isomerisation:



(15.0 mdyn $Å^{-1}$ for the *s-cis*-isomer and 16.1 mdyn $Å^{-1}$ for the *s-trans*-isomer), while the C=C bond changes little (36); unfortunately the authors did not estimate K(C–C) and K(C=C, C=O).

The non-empirical calculation of the force constants for methylamine and a series of other simple molecules[37–39] permitted the assignment of certain lines concerning which contradictory view had been expressed or at least to reject the earlier explanations; for example it was established that the 777 cm^{-1} band in the spectrum of HNCO refers to an out-of-plane vibration, while in the hydroxylamine spectrum the torsional vibration band should be in the region of ~1300 cm^{-1}.

The estimates of the strengths of bonds involving the metal atom in salts in the absence of intermolecular interaction are of interest. According to calculated data[40], the coefficient K(Li–C) for an isolated LiCN molecule should be lower by a factor of 3–4 than for the bonds with the cyano-group in the H–CN, Cl–CN, and H_3C–CN molecules.

According to Schlegel et al.[21], the force constants differ significantly for the C–H bonds oriented in different ways relative to the unshared electron pair of the neighbouring heteroatom. Predictions of the spectrum of vinylborane, which is virtually impossible to determine experimentally, have been made on the basis of the calculated force constants and frequencies[41].

During recent years attempts were made to use quantum-chemical calculations of vibrational frequencies for the evaluation of the partition functions and for the determination from the latter of the entropy contribution to the free energy. The spectra of stable molecules can be most simply determined experimentally, but quantum-chemical methods are applicable also to unstable compounds and to transition states (see, for example, Yoshioka et al.[43]); at the same time they can yield information about the frequencies of unobserved transitions. Thus the entropy contribution to the activation energy can be estimated from calculated frequencies and extremely fine kinetic effects can be interpreted. The first studies showed that the accuracy of the method is entirely sufficient for this purpose; thus data have been obtained for the primary kinetic isotope effect in the reaction $CH_2=CH-CH_2COOH \rightarrow CH_3CH=CH_2 + CO_2$, which agreed well with experiment[25].

In connection with the foregoing, it must be emphasised that the results of quantum-chemical calculations cannot as yet characterise the force field and the frequencies ω with an accuracy equal to that of the experimental determination, but they are extremely useful for line assignments and the combination of calculated and experimental data leads to a more complete and reliable description of the spectrum. The calculated *relative* values are more reliable and can assist in interpreting the comparatively small differences between the frequencies of similar molecules, which cannot always be done by other methods.

By combining quantum-chemical methods with the usual methods involving calculation from experimental frequencies, it is possible to achieve a significant refinement of the force field (see the examples in the literature[42,44,55]).

IV. THE INTENSITIES OF INFRARED ABSORPTION BANDS

The integral intensity of a fundamental infrared absorption band is known to be proportional to the square of the derivative of the molecular dipole moment $\partial\mu/\partial Q$. The origin of the dependence of the dipole moment on Q is associated both with the displacement of the atoms carrying a charge and with the changes in the charges themselves (or in the populations of the atomic orbitals).

In order to calculate the intensity, it is sufficient to evaluate the dipole moments for the equilibrium and non-equilibrium values of Q, which does not present significant technical difficulties, although it does require the knowledge of the vibrational mode. Among the semiempirical methods, best agreement with experiment is achieved with the aid of the CNDO/2 method and a somewhat worse agreement is obtained using the MINDO/3 and INDO methods. An important feature of the quantum-chemical methods is the possibility of determining the signs of the derivatives of the dipole moment. If the derivatives are fairly large, their signs are found to be the same whatever the method, including the non-empirical methods, and they can be regarded as more or less reliable; the differences in sign have been obtained only for certain deformation vibrations of the C–H bonds.

Table 3. Derivatives of the dipole moments with respect to symmetry coordinates (D $Å^{-1}$).

Symmetry coordinate	CNDO/2 (Ref.45)	CNDO/2 (Ref.125)	MINDO/3 (Ref.45)	NMLB* (Ref.125)	Experimental
		CH_4			
S_3 (stretch)	−0.625	−0.74	−1.39	−0.97	0.704
S_4 (deformation)	0.24	−0.34	0.29	0.33	0.387
		C_2H_4			
S_7 (deformation)	2.37	1.50	0.59	2.35	1.805
S_8 (stretch)	−1.23	−1.17	−2.03	−0.91	0.725
S_{10} (deformation)	−0.392	−0.33	0.05	−0.05	0.350
S_{11} (stretch)	0.859	0.69	0.94	0.79	0.605
S_{12} (deformation)	0.043	0.08	−0.13	0.30	0.269

*Calculation by a non-empirical method in terms of a large basis set.

The results of calculations by different methods for methane and ethylene (Table 3) and other compounds[45–50] have shown that the quantum-chemical methods make it possible to obtain a semi-quantitative agreement with experiment and to determine which lines should be intense, which should be weak, and which should not be observed at all. Such data are sufficient for the solution of many spectrochemical problems. The differences between the intensities of lines associated with isotypical vibrations can

be calculated with a high degree of accuracy for a series of molecules with similar structures. Thus a fairly satisfactory correlation with experiment has been obtained for the C=C stretching vibration bands in the spectra of different ethylene derivatives $H_2C=CHX$, although the intensities differed in this instance by a factor of 5–10;[51] here it would be appropriate to take the next step and to give a well-founded explanation of the higher intensity of the bands of molecules containing electron-donating groups X.

The simplest but as yet insufficiently tested procedure for increasing the accuracy of the calculation of the line intensities involves the selection of scale factors or increments. This method has been used to find derivatives of the dipole moments of acetylene, ethylene, and ethane. In calculations by the non-empirical method in terms of a minimal basis set the derivatives were found to be too low to approximately the same extent; their multiplication by 1.2 led to quite acceptable results and to an adequate agreement with experiment[52].

Problems of increasing the accuracy of the calculation of the vibrational mode for the atoms and of extending the basis set for the calculation of the wave functions by including polarising orbitals in the set (p orbitals for the H atom and d orbitals for the C and O atoms) and also of allowing for electron correlation stand in the way towards a more rigorous and accurate calculation of the infrared band intensities (without introducing corrections)[53].

V. PROCEDURES FOR THE INVESTIGATION OF THE STRUCTURES OF MOLECULES IN ELECTRONICALLY EXCITED STATES

The available information about the electronic structures and properties of organic molecules in excited states is extremely scanty. Such substances are comparatively unsusceptible to experimental study and the possibility of resorting to quantum-chemical methods is very important. It is noteworthy that the study of excited states is very important not only for the characterisation of the optical properties of molecules but also for understanding the characteristics and mechanisms of many chemical (primarily photochemical) reactions.

The Hartree–Fock approximation for molecules with closed shells, described in Section II, makes it possible to calculate the electronic wave function of the ground state Φ_0. In the study of electronically excited states, certain modifications must be introduced into the computational scheme. The simplest modification is the approximation of virtual orbitals[54], in which all the one-electron molecular orbitals are calculated by the standard Hartree–Fock method for the ground state, each occupied molecular orbital containing a pair of electrons with opposed spins. After the calculation of the coefficients (adjusted for self-consistency) of the expansion of the molecular orbitals with respect to atomic orbitals the energy of the molecular orbital, and the total molecular energy, one of the electrons is "transferred" from the occupied to the vacant orbital. The energy of this transition ($m \to r$) is calculated as the difference between the energies of the electron in these orbitals, since all the remaining molecular orbitals are assumed to be unaltered (which can be regarded as a fairly rough approximation).

In order to take into account the changes in the molecular orbitals of electronic excitation, we shall make use of the method of configuration interaction (CI). In this method the wave functions $\Phi_{m \to r}$ of excited singlet states, calculated in terms of the approximation of virtual orbitals

$$\Phi_{m\to r} = \text{const} \cdot \det|\varphi_1(1)\alpha(1')\varphi_1(1')\beta(1')\ldots\varphi_{m-1}(m-1)\times \cdot\times\alpha(m-1)\varphi_{m-1}(m-1)'\beta(m-1)'\varphi_m(m')\beta(m')\ldots \ldots\varphi_n(n)\alpha(n)\varphi_n(n')\beta(n')\varphi_r(r)\alpha(r)|$$

constitute the basis set. Linear combinations of these functions

$$\Psi_{q\to t} = \sum_{mr} C_{mr}^{qt}\Phi_{m\to r}$$

give rise to more accurate wave functions of the excited states. The subscripts and superscripts m, r, q, and t can vary from 1 to N, where N is the number of atomic orbitals in the basis set adopted. The coefficients C_{mr}^{qt} are determined by the diagonalisation of the matrix made up of the elements $\langle\Phi_{m\to r}|H|\Phi_{m'\to r'}\rangle$. The functions $\Phi_{m\to r}$ are of the one-determinant type, while the functions $\Psi_{q\to t}$, with CI, are of the multideterminant type. However, for the majority of excited states the main contribution to $\Psi_{q\to t}$ comes from only a single one-determinant function $\Phi_{m\to r}$, while others introduce only a small correction reflecting the changes in the molecular orbital on excitation.

Other methods widely used to study the geometry and electronic structure of molecules in the excited state are the restricted and unrestricted Hartree–Fock methods for open shells and the Dewar half-electron method.

In calculations by the restricted Hartree–Fock method on systems with open shells equations of types (3) and (4) include non-diagonal Lagrange coefficients[2], and their solution is more complex than for systems with closed shells. However, entirely acceptable procedures have been proposed for their solution[56–59], which made it possible to apply the method on a fairly large scale in non-empirical calculations of the geometry of excited states.

When the unrestricted Hartree–Fock method is used, two different sets of linear combinations of atomic orbitals, corresponding to electrons of different spins, are introduced for each electron pair. Each electronic state is described by a specific set of coefficients defining the electron population of the molecular orbitals. The coefficients of the expansion of MO and AO are determined from the system of equations obtained by Pople and Nesbet[60]. The principal deficiency of the method consists in the fact that the wave function obtained does not, strictly speaking, represent the eigenfunction of the square of the spin operator and is an inaccurate solution, which can be improved only by introducing an additional laborious procedure.

The Dewar half-electron method[61] is based on the standard Roothaan equations for molecules with closed shells (where there are two electrons in each molecular orbital) but with an altered number of electrons in two molecular orbitals in the calculation of the bond charge and order matrix P_{ij}. This description of the excited state with retention of Eqn.(4) for F_{ij} implies in essence that the molecular orbitals, occupied by a single electron in the standard Roothaan method, are populated by two "halves" of an electron with opposed spins. F_{ij} then incorporates the matrix elements of the Coulombic interaction of the electron halves and the exchange interaction between the unpaired electrons is incorrectly taken into account. The necessary corrections for this can be introduced into the final total energies, retaining the standard Roothaan expressions for F_{ij}. In this case the usual programs for molecules with closed shells are less altered on passing to the study of excited states. In the determination of the coefficients for the expansion of the molecular orbitals with respect to the basis set of atomic

orbitals one then minimises an inaccurate expression for the total energy, but the associated errors are small and do not have a significant influence on the results of the calculation.

The advantages and disadvantages of each of the above methods have not yet been adequately investigated, but they are apparently entirely suitable for calculations of the geometries and electronic structures of excited molecules. Examples of calculations of the geometries of excited singlet states are presented in Table 4. It is noteworthy that Table 4 lists the absolute geometrical parameters, whereas for spectroscopic purposes their changes on excitation are mainly required; the latter are reproduced much less accurately by quantum-chemical methods. For other examples, see the literature[62-68]. From the standpoint of computer time, the Dewar half-electron method[68] is the most economical among those enumerated above and can be recommended for calculations on large molecules.

Table 4. The geometry of molecules in the lowest electronically excited state[61,65].

Parameter*	CNDO/2 (virtual MO)	CNDO/2 with allowance for CI	OST-4G with allowance for CI	OST-4-31G with allowance for CI	MINDO/3 in combination with RHFM**	MINDO/3 ***	Experimental
HCN							
R_{CN}, Å	1.30	1.30	1.37	1.30	—	—	1.30
H-C-N angle, deg	129	127	112	127	—	—	125
H_2CO							
R_{CO}, Å	1.28	1.28	1.31	1.27	1.26	1.25	1.32
α, deg	0	31	28	15	38	29	31
HC≡CH							
R_{CC}, Å	1.34	1.33	1.37	1.37	1.35	1.35	1.39
H-C-C angle, deg	137	136	121	125	124	124	120

*Here R is the interatomic distance and α the angle between the C=O bond and the CHC plane.

**Restricted Hartree–Fock method.

***In combination with the "half-electron" method.

VI. QUANTUM-CHEMICAL CALCULATIONS OF THE FREQUENCIES AND PROBABILITIES OF ELECTRONIC TRANSITIONS

The quantum-chemical calculations of the geometry and of the distribution of electron density for excited states, examined above, can be regarded as successful, since even semiquantitative results are extremely useful. However, for the calculation of electronic absorption spectra, it is necessary to have more accurate wave functions and, despite their laborious nature, variants taking into account the configuration interaction are used nowadays for this purpose.

Calculations in terms of the CNDO/S valence approximation with allowance for CI are most widely used to investigate the electronic absorption spectra of molecules containing systems of conjugated π-bonds[11,12]. Several modifications of the method have been proposed, differing slightly from one another in the choice of the empirical parameters but leading to fairly similar final results. The errors in practical calculations of the energies of $\pi \rightarrow \pi^*$ electronic transitions do not exceed several tenths of electron-volts even for fairly complex molecules (Table 5). The accuracy is lower for the $n \rightarrow \pi^*$ transitions and the energies obtained are in most cases too low. The latter is apparently associated with the use of the CNDO approximation in which no account is taken of a series of interaction integrals between electrons making a significant contribution to the energy of the $n \rightarrow \pi^*$ transitions. The singlet–triplet splitting for n, π^* excited states is then found to be zero, although in reality for certain compounds it reaches 1 eV.

Table 5. Calculation of the electronic absorption spectra by the CNDO/S method[11,12].

Transition	Transition energy, eV		Oscillator strength	
	calc.	expt.	calc.	expt.
Benzene				
$^1B_{2u}$ $(\pi \rightarrow \pi^*)$	4.8	4.9	0	0.002
$^1B_{1u}$ $(\pi \rightarrow \pi^*)$	6.1	5.9	0	0.1
$^1E_{1u}$ $(\pi \rightarrow \pi^*)$	6.9	6.7	1.2	0.7
Chlorobenzene				
$^1B_1$ $(\pi \leftarrow \pi^*)$	4.8	4.8	0	0.005
$^1A_1$ $(\pi \rightarrow \pi^*)$	6.0	6.0	—	0.2
$^1B_1$ $(\pi \rightarrow \pi^*)$	6.7	6.7	0.3	0.47
$^1A_1$ $(\pi \rightarrow \pi^*)$	6.8	6.9	1.7	0.73
Pyridine				
$^1B_2$ $(n \rightarrow \pi^*)$	4.4	4.3	0.006	0.003
$^1B_1$ $(\pi \rightarrow \pi^*)$	5.0	4.8	0.06	0.04
$^1A_1$ $(\pi \rightarrow \pi^*)$	6.2	6.2	0.08	0.20
$^1B_1$ $(\pi \rightarrow \pi^*)$	7.2	7.0	0.8	1.3

Semiempirical methods have been little used for the calculation of the energies of $\sigma \rightarrow \sigma^*$ transitions; the accuracy obtained using the existing parametrisations should be low and one may expect qualitative rather than quantitative results. One should remember that in semiempirical methods one normally employs a minimal basis set and this precludes the calculation of the parameters of the Rydberg transitions (to orbitals with large quantum numbers), which usually occur in the region of $\sigma \rightarrow \sigma^*$ electronic transitions and can be mixed with them.

In calculations on the excited states and electronic absorption spectra by non-empirical methods one has to have much larger basis sets than for the calculation of the properties of the molecular ground state. The attempts to select small basis sets have led to agreement with experiment only for individual electronic transitions in a limited range of compounds. This is because the change in the distribution of electron density on excitation is not reproduced with the necessary accuracy by a simple alteration of the population of the molecular orbitals or even by a transition to their linear combinations. In other words, the basis set of atomic orbitals selected for the ground state is unsatisfactory for the excited state. On excitation, the electron cloud usually expands and this has a marked influence on the matrix elements for the interaction of electrons and nuclei. In order that the wave function expanded in terms of the basis set of atomic orbitals (i.e. represented by a linear combination of atomic orbitals) should reproduce this expansion, the basis set must be modified—the orbital exponents must be altered somewhat or additional diffuse orbitals must be included. The nature of the expansion of the electron cloud is specific to each $0 \rightarrow e$ electronic transition and the only rational method of improving the basis set involves an increase of the number of atomic orbitals.

The introduction of very large basis sets and allowance for the contributions of all singly and doubly excited configurations greatly extend the scope of the calculation and make it possible to evaluate the energies of electronic transitions to within 0.2–0.5 eV. However, at the present time this is possible only for small molecules, since the difficulty of the calculations increases very rapidly with increase of the number of atoms. The results of such calculations of the spectra of ethylene, butadiene, benzene, and certain other compounds with simple molecules have been published in a review[69].

Non-empirical methods are most widely applied in calculations on Rydberg transitions[69–72]. For simple molecules, it has been possible to calculate, in good agreement with experiment (±0.1 eV), the positions of the absorption bands, but their assignments are not always reliable, since the Rydberg bands are very close to one another (even in triatomic–penta-atomic molecules up to 10 transitions may be located in the region of 7–8 eV). The non-empirical methods lead to appreciably high energies of the lowest $\pi \rightarrow \pi^*$ transitions (error up to 1 eV).

In practice calculations of the electronic absorption spectra of organic compounds extend over a region of not more than 8–10 eV. For a more remote region, the difficulty of the calculations increases greatly owing to the necessity to take into account highly excited configurations.

The oscillator strengths of the electronic transitions are calculated less accurately in all the methods than the transition energies and the results can differ severalfold from the experimental data. The requirements for the accuracy of the wavefunctions are then particularly stringent and the small errors associated with the selection of the basis set can be markedly reflected in the results; in practice it is necessary to take into account the contributions of a still greater number of excited configurations. However, the oscillator strengths of the observed $0 \rightarrow e$ transitions can differ by several orders of magnitude; under these conditions, even semiquantitative estimates are sufficient for the prediction of the overall form of the absorption spectrum and for the interpretation of the individual bands.

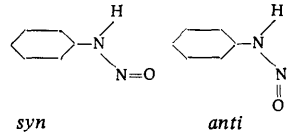
The results of the calculation can usually be compared with experiment only for a few (long-wavelength) electronic transitions. The majority of transitions are located in a region difficult to investigate experimentally (<1500 Å) and the lack of experimental data for such transitions hinders the direct estimation of the accuracy of the computational methods. However, indirect procedures can be used for this purpose. The electronic polarisability can be evaluated from the oscillator strengths and frequencies ν_e of the $0 \rightarrow e$ transitions calculated by a quantum-chemical method and the results can be compared with experimental data. Polarisability calculations have been carried out for many types of molecules[70–75] and for the majority of these a sufficient agreement with experiment has been obtained, which shows indirectly a satisfactory accuracy of the calculation of the parameters of the absorption bands over a wide range of the spectrum.

When the results of the calculation of oscillator strengths are used to infer the structure of complex molecules, one must not underestimate their approximate nature. In this connection mention should be made of calculations for 4-nitro-*N*-benzylideneaniline[76]; within the framework of the comparison made, the results correspond to the arrangement of the two benzene rings in perpendicular planes, which is extremely unlikely. Examples of the application of calculations of oscillator strengths, dipolar and quadrupolar polarisabilities, and hyperpolarisability have been described[77–82].

VII. THE APPLICATIONS OF QUANTUM-CHEMICAL CALCULATIONS TO THE EXCITED STATES OF ORGANIC MOLECULES

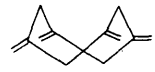
The quantum-chemical calculations of the electronic structures and geometries of electronically excited molecules are widely used to interpret experimental data and to assign ultraviolet absorption bands, to establish a relation between absorption spectra and the structure of the molecule and its conformation, and also to investigate the reactivities of electronically excited molecules in photochemical processes[83–90].

We shall consider several examples. In the absorption spectra of certain organic compounds the characteristic long-wavelength bands were previously tentatively assigned to charge-transfer transitions but this could be proved and the contribution of charge transfer could be estimated only by quantum-chemical calculations. In particular, it has been established for *N*-alkyl-*N*-nitrosoaniline and its alkyl derivatives[83] that excitation in the first (long-wavelength) absorption band leads to an electronic transition in the benzene ring (^1L_b), while excitation in the second band leads to an electronic transition mainly in the NNO group; the absorption of light whose frequency corresponds to the third band gives rise to an electron density distribution with transfer of more than half of the electronic charge from the NNO group to the benzene ring, while absorption in the fourth band modifies the wave functions in the region of the benzene ring (^1L_a). It follows from the calculation that the charge-transfer band should be observed experimentally only for the *anti*-isomer, while for the *syn*-isomer it should be close to the more intense ^1L_a band and should be masked by the latter:



syn *anti*

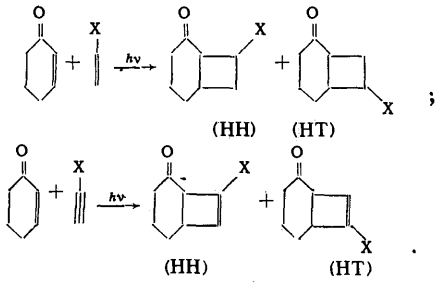
The experiments have shown that certain non-conjugated polyene compounds (adamantane derivatives) with a fixed relative orientation of two double bonds of the type



have an intense absorption band at ~230 nm (while for monoolefins the first intense band is located in the region <200 nm). Non-empirical calculations have led Braverman et al.[84] to the conclusion that this band is due to the electronic transition between the components of the split π and π^* levels, caused by the mutual influence of the double bonds through space. This influence also leads to the stabilisation of the excited state, while interaction via methylene bridges (with participation of the σ orbitals of the C–H bonds) affects the energies of the highest occupied orbitals and the symmetries of the molecular wave functions; the latter explains the high intensity of the absorption band. A simpler system with two weakly interacting C=C bonds (norbornadiene) has been investigated[85]; the contributions of charge transfer were estimated for each excitation level and the influence of hyperconjugation involving the bridging atoms on the $^1A_1 \rightarrow {}^1B_2$ transition was noted.

No less interesting results can be obtained in the study of photochemical reactivity. Thus the stereospecificity of the photochemical addition of acetylene and ethylene derivatives (HC≡CX and $H_2C=CHX$) to α,β-unsaturated

ketones has been considered[86]. Experimental studies on the reaction led to unusual results; it was found that certain acetylene and ethylene derivatives form products in which the carbonyl group of the ketone and the substituent X are directed to one side ("head to head", HH), while in others, i.e. in the presence of a second substituent X, they are directed to different sides ("head to tail", HT); in the third case the stereospecificity vanishes; examples of the reaction mechanisms are given below:



According to the results of the calculations the ground and excited (triplet) states by the CNDO/2 method, the above difference can be accounted for by the fact that the stereospecificity of the reaction of ethylene derivatives is due mainly to the interaction between the π-electron orbitals of the C=C bonds of the reacting molecules, while in the case of acetylene derivatives it is caused by the dipole–dipole interaction. The absence of stereospecificity in the addition of acetylene derivatives containing only the highly polar CHO and COOH substituents is associated with the fact that the component of the dipole moment perpendicular to the direction of the C ≡ C bond predominates in these derivatives[86].

Interesting data concerning the changes in molecular geometry on electronic excitation have been obtained with the aid of non-empirical methods (Fig.1). It is at present impossible to obtain such information in other ways. In another investigation[89] it has been shown that all the bond lengths in the pyrazine ring increase as a result of the $\pi \rightarrow \pi_1^*$ electronic transition, while in the $n \rightarrow \pi_1^*$ transition the C–C bonds become shorter.

The use of quantum-chemical methods in the study of optical activity is particularly appropriate for molecules with conjugated or highly interacting bonds where the approximation of weakly bound subsystems (molecular fragments) is unsuitable. As an example, we may note the calculations of the rotatory power of the $n \rightarrow \pi^*$ electronic transitions in dioxan-1,4-dione and its methyl derivatives, as a result of which it was possible to estimate separately the contributions of the asymmetric substitution in the ring and of the dissymmetry (chirality) of the ring itself in each conformer[87].

VIII. THE INTENSITIES OF THE COMPONENTS OF VIBRONIC TRANSITIONS

The calculation of the intensities of the components of the vibrational structure is of primary important for the characterisation of the overall form of the bands in the electronic absorption and fluorescence spectra and also for the calculation of the Raman line intensities.

In specific calculations it is usually assumed that, in the overall wave function of a molecule, it is possible to distinguish the electronic and vibrational components Ψ_e and $\prod_a u(Q_a)$. The transition moment $00 \rightarrow ev$ involving a change in the electronic and vibrational states can then be represented by the following expression of:

$$\mathbf{M}^{00\rightarrow ev} = \int \ldots \int \prod_a u_{00}(Q_a)\, M^{0e}\, u_{ev}(Q_a)\, \mathrm{d}Q_i, \qquad (7)$$

in which the integration is carried out with respect to all the Q_a, M^{0e} is the moment of the $0 \rightarrow e$ transition determined by the function Ψ_0 and Ψ_e, and u_{00} and u_{ev} are the nuclear wave functions of the initial (00) and final (ev) states. In principle, M^{0e} is a function of the normal nuclear coordinates; M^{0e} can be expanded in series in powers of Q, retaining only its first terms in view of the rapid convergence of the series. The dependence of M^{0e} on the coordinates Q_{as} of the antisymmetric atomic vibrations largely determines the distribution of intensities in the series of components $\nu_{e0} + n\nu_{as}$ of the absorption band. However, for symmetrical modes, this type of dependence is of secondary importance and is frequently disregarded; the calculation of the intensities of the components of vibronic transitions then requires the calculation of M^{0e}, the molecular geometry, the frequencies and modes of the atomic vibrations, and the nuclear wave functions for the ground and excited states.

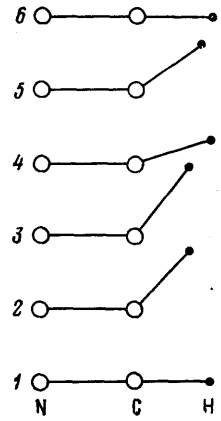


Figure 1. The geometry of the HCN molecule in the ground and excited states (the energies of the states are given in brackets in eV): *1*) ground state (0.0); *2*) $^1A''$ (6.48); *3*) $2^1A'$ (6.78); *4*) $2^1A''$ (7.52); *5*) $3^1A'$ (7.85); *6*) $3^1A''$ (8.97).[80]

Calculations of the intensity taking into account the $M^{0e}(Q)$ relation and, if necessary, the differences between the potential energy curves for the molecule in the ground and excited electronic states, carried out by non-empirical methods for formaldehyde and other molecules[91–94] and by semiempirical methods for benzene, naphthalene, benzoperylene, formaldehyde, and benzaldehyde[95–100], led to a fairly satisfactory agreement with experimental data (Table 6). The results made it possible to interpret certain vibronic bands in the absorption spectra; in particular, it has been shown[92] that the electronic transition $n \rightarrow \pi^*$ in the N_2H_2 molecule is combined with the excitation not only of the fully symmetrical modes but also of the antisymmetric stretching vibration of the N–H bonds, giving rise to a whole series of the corresponding components in the vibrational structure of the absorption band.

According to Herzberg and Teller, the $M^{0e}(Q)$ relation can be expressed in terms of a set of coefficients h_{es}, which determine the mixing of the wave functions Ψ for different electronic states (e and s) as the normal coordinate Q is varied. In this connection, some workers arrived at the erroneous idea that a simple quantum-chemical calculation of the probability of vibronic transitions in terms of mixing coefficients is possible. However, such calculation requires the evaluation of the overlap integrals of the multideterminant electronic wave function of the excited state of a deformed molecule (i.e. for $Q \neq 0$) and the wave functions of all other states corresponding to the equilibrium positions of the atoms in the ground state ($Q = 0$). The exact evaluation of these integrals is difficult owing to the incompleteness of the sets of atomic orbitals used in practice, so that the molecular orbitals corresponding to $Q = 0$ and $Q \neq 0$ are constructed in terms of different basis sets (displaced relative to one another). Under these conditions, it is generally speaking impossible to expand the function Ψ of a deformed molecule in terms of the atomic orbitals corresponding to the equilibrium molecular geometry. In order to calculate the coefficients h_{es}, it is therefore necessary to introduce a series of approximate assumptions[95]. On the other hand, direct calculation of the derivatives $\partial M^{0e}/\partial Q$ does not require the introduction of additional assumptions and is fairly easy[97].

Table 6. Calculation of the oscillator strengths of vibronic transitions ($00 \rightarrow ev$) corresponding to four vibrational modes in benzene by the CNDO/S method (the results of calculations with the aid of the Herzberg–Teller expansion described by Roche and Jaffe[95] are indicated in brackets).

ω, cm^{-1}	$^1B_{2u}$ transition			$^1B_{1u}$ transition		
	calc. (Ref.97)	calc. (Ref.99)	expt.	calc. (Ref.97)	calc. (Ref.99)	expt.
606	$5\cdot10^{-4}$	$8\cdot10^{-4}$	$1.4\cdot10^{-3}$	$1.6\cdot10^{-2}$	$1.3\cdot10^{-2}$	$1.9\cdot10^{-2}$
1595	$2.5\cdot10^{-4}$	$8\cdot10^{-5}$	10^{-4}	$6.8\cdot10^{-2}$	$1.4\cdot10^{-1}$	$7.5\cdot10^{-2}$
3047	$8\cdot10^{-6}$	$6\cdot10^{-5}$	0	$7\cdot10^{-4}$	10^{-3}	0
1177	$4\cdot10^{-5}$	$2\cdot10^{-6}$	0	$6\cdot10^{-3}$	$1.2\cdot10^{-2}$	0
Overall oscillator strengths						
	$8\cdot10^{-4}$	$9\cdot10^{-4}$ ($9\cdot10^{-4}$)	10^{-3}	$9\cdot10^{-2}$	$2\cdot10^{-1}$ ($2\cdot10^{-1}$)	$9\cdot10^{-2}$

IX. CALCULATION OF LINE INTENSITIES IN RAMAN SPECTRA UNDER CONDITIONS REMOTE FROM AND CLOSE TO RESONANCE

The intensity of the Raman lines and the line excitation spectra (the dependence of the intensity on the frequency of the exciting light ν) can be calculated subject to greater or smaller limitations, using the classical, semi-classical, or quantum theories. In the "polarisability theory" designed for cases very remote from resonance the line intensity I_a is determined by the set of derivatives of the components of the molecular electronic polarisability tensor α with respect to the coordinate Q_a. The polarisability theory treats α as a single-valued function of Q (and corresponds to ideas concerning a molecule with stationary nuclei in any specified positions Q) but it does not define the origin of the $\alpha(Q)$ relation. The latter is described within the framework of the semiclassical theory[101] as a consequence of the dependence on Q of (a) the Cartesian components $M^{0e}(Q)$ of the dipole moment of the electronic transition $0 \rightarrow e$ made up of the electronic wave functions $\Psi(Q)$ and (b) the frequency ν_e. The contributions of all the electronic excitation levels e are then added together (cf. the book of Tang and Albrecht[102] where incorrect information is given on this subject).

The origin of the $M^{0e}(Q)$ relation in the vibronic theory of Tang and Albrecht[102] is inferred by considering the matrix of the coefficients h_{es}, which describes the mixing of the electronic wave functions of the levels e and s when the nuclei are displaced from the equilibrium positions (see below). In the simplest case

$$M^{0e}(Q) \simeq M^{0e}(0) + Q \sum_{s \neq e} \frac{h_{es} M^{0s}(0)}{E_e(0) - E_s(0)},$$

where $E_e(0)$ and $E_s(0)$ are the molecular energies in the states e and s for $Q = 0$.[103]

All the Cartesian components $(\rho\sigma)$ of the polarisability tensor for any positions of the atomic nuclei can be calculated in terms of the adiabatic approximation of the second order perturbation theory by the formula

$$\alpha_{\rho\sigma}(Q) = \frac{1}{h} \sum_e \left[\frac{M_\sigma^{0e} M_\rho^{e0}}{\nu_e - \nu} + \frac{M_\rho^{0e} M_\sigma^{e0}}{\nu_e + \nu} \right]. \quad (8)$$

The introduction of the dependence of M^{0e} and ν_e on Q compensates to some extent the lack of summation of the contributions of the individual vibrational sublevels ev. The wave functions Ψ necessary for the calculation of the polarisability are determined by quantum-chemical methods; the derivatives with respect to Q are usually found by numerical differentiation.

Calculations of the Raman line intensity by Eqn.(8), which reflect in some form the factors of the semiclassical theory $\nu_e(Q)$ and $M^{0e}(Q)$, have been carried out for many simple molecules (H_2, Cl_2, methane, ethane, ethylene, acetylene, dimethyl ether, etc.). Analysis of the results obtained by different LCAO-MO SCF methods[26,29,70,104–110] showed that for polyatomic molecules they reproduce the distribution of intensities in a manner which is qualitatively correct but extremely approximate, and that non-empirical methods in terms of basis sets of moderate size of the type of OST-4-31GF do not result in a perceptible increase of accuracy compared with semiempirical methods.

More accurate but more laborious non-empirical calculations, using extended basis sets with polarisable orbitals and taking into account electronic correlation, have led to a very satisfactory agreement with experiment for the simplest molecules[111,112]; thus the derivatives of the polarisability of the hydrogen molecule[111] are $\alpha'_\parallel = 1.78$ and $\alpha'_\perp = 0.83$, while the corresponding experimental values are 1.69 and 0.85 respectively. The closeness to the experimental data is not surprising, since virtually exact wave functions were obtained in the relevant investigation[111]; unfortunately such calculations are virtually impossible for complex molecules.

Studies on the simplest hydrocarbons (methane and ethylene) by CNDO/2 methods resorting to the vibronic theory[113,114] led to the conclusion that the $\nu_e(Q)$ relation predominates for lines associated with symmetrical vibrations and also that the mixing of the electronic wave functions Ψ_e with the function Ψ_0 of the ground state (which is usually neglected) makes a significant contribution. However, the polarisability derivatives obtained are in poor agreement with experimental data and at the same time differ markedly from the results of the calculation within the framework of the polarisability theory. The

discrepancies with experiment are to a large extent associated with the insufficiency of information about the highest levels e and with the approximate nature of the calculation of the coefficients h_{es} from the formula of Murrell and Pople[95,115].

Regardless of the foregoing, one may state in a more general form that the application of the vibronic theory in the quantum-chemical calculations of Raman line intensities is undesirable, since the $M^{0e}(Q)$ relation can be calculated directly and much more readily and accurately without introducing the h_{es} matrix and without any additional approximations by evaluating analytically or numerically all the necessary integrals in Eqn.(8); this does not require information about all the levels s, which can be mixed with the level e. However, the calculation of h_{es} is necessary if it is required to elucidate the origin of the $M^{0e}(Q)$ relation.

Thus, in order to calculate the intensity, it is sufficient to carry out independent calculations of M^{0e} and ν_e for several values of Q and to estimate from these data their derivatives with respect to Q and then calculate the derivatives of the polarisability from the formula of the semiclassical theory. Similar calculations for ethylene in the CNDO/S valence approximation with allowance for the contributions of all the singly excited configurations[109] led to estimates of the form of the Raman line excitation spectra and by no means fully confirmed the conclusions of the study quoted above[114]; it follows from the calculations of Burshtein and Shorygin[109] that, following Raman excitation in the visible part of the spectrum, the $M^{0e}(Q)$ relation predominates for all the C–H lines, while the $\nu_e(Q)$ relation predominates for the C=C line. The main contribution for the C=C line comes from the long-wavelength electronic transitions $\pi \rightarrow \pi_1^*$, while for other lines the transitions in the region of ~1000 Å, localised predominantly at the C–H bonds, are the most significant.

Calculations of polarisability for several values of Q for each molecule require a large amount of computer time. To reduce it, it has been suggested that one calculates the derivatives with respect to the external electric field strength of the gradient (with respect to Q) of the potential energy of the molecule present in this field; these derivatives are found only for the equilibrium geometry of the molecule[116].

We may note that the calculation of the derivatives is generally speaking not obligatory; one can resort to the relation $2\alpha_{01} \cong \alpha(Q_0) - \alpha(-Q_0)$, which leads to a somewhat greater accuracy and requires the calculation of α for only two values of $Q = \pm Q_0$, where Q_0 is the zero point amplitude[117].

The use of a minimal basis set in calculations of the polarisability and intensity is fairly problematical. Some investigators[110] insist on introducing extended basis sets of atomic orbitals with inclusion of polarising atomic orbitals (2p and 3p for hydrogen atoms and d for atoms of elements in the Second and Third Periods) and diffuse orbitals. One must agree with this if one is dealing with non-empirical calculations; however, when semiempirical methods are employed, a rational selection of the parameters determining the interaction of the nuclei and electrons makes it possible to compensate to a large extent for the incompleteness of the basis set, because ultimately one needs to determine not the atomic wave functions themselves but the matrix elements calculated using these functions. Whereas in the non-empirical methods of calculation the selection of the basis set to a large extent determines the set and magnitudes of the matrix elements for the interactions of the electrons and nuclei, in semiempirical methods the selection of the basis set is less significant in this respect and the extension of the basis set is associated with a certain arbitrary element in the choice of the parameters for atomic orbitals with large quantum numbers (polarising orbitals) and at the same time does not lead to an appreciable improvement of the results; for these reasons, it is not desirable.

Instead of introducing polarising functions into the computational scheme, it is possible to introduce at some stage corrections in the form of atomic increments[75]. In principle, it is thus possible to correct, for example, the matrix elements of the interaction, but it is simpler to select polarisability increments. The latter are most significant for hydrogen atoms and they can be determined in this instance from experimental data for the H_2 molecule. In calculations using the minimal basis set (without corrections) the perpendicular components of the polarisability of H_2 and its derivative are found to be zero and their true values, determined experimentally, are used as the increments.

The principal difficulty in the calculation of the polarisability by Eqn.(8) consists in the need to calculate the parameters of all the electronically excited states—the energies, the wave functions Ψ_e, and the matrix elements M^{0e}. This difficulty can be in many instances obviated by resorting to the finite perturbation theory[104–106] or by using a variational procedure[118,119], for which it is sufficient to know the wave function Ψ_0 of the ground state. Bearing in mind that calculations by the LCAO-MO method are more accurate for Ψ_0 than for Ψ_e, under certain conditions it is possible to count on a higher accuracy of the determination of the polarisability[120].

Only the tensor of the *static* electronic polarisability can be calculated by the finite field methods in the perturbation theory. To evaluate this tensor, an electric field is introduced into the electronic Hamiltonian of the molecule. In the CNDO valence approximation it is sufficient for this purpose to add to the diagonal elements of the Fock matrix terms of the type $-eE_x x_a$ and to the non-diagonal elements of the type $-eE_x\langle s_a|z|p_{xa}\rangle$, where E is the electric field strength and s_a and p_{xa} are atomic orbitals of the s and p type of the atom a. Having calculated in this way all the Cartesian components of the dipole moment of the molecule in the ground state with (μ^*) and without (μ^0) an external field, we obtain the following expression for the specified positions of the atoms:

$$\alpha_{\rho\sigma}(Q) = (\mu_\rho^* - \mu_\rho^0)/E_\sigma.$$

The Raman line intensities for methane, ethylene, tetrachloroethylene, and other simple molecules were calculated from the polarisabilities and their derivatives found by this procedure. The calculations of μ were performed within the framework of the extended Hückel method, by the CNDO/2 and INDO methods, and also by non-empirical methods in terms of very large Gaussian basis sets with polarising functions[104–106,116].

The applications of the finite perturbation theory are not associated with cumbersome calculations and they can therefore be extended to more complex polyatomic organic molecules. The results for cyclopropenone are compared with experimental data in Fig.2.

It must be emphasised that static polarisability data can be used only when the frequency of the exciting light is very remote from ν_e; the Raman intensities calculated directly via derivatives of the static polarisability have generally speaking no physical significance although they can differ only slightly from values found for low frequencies of the exciting light ($\nu \ll \nu_e$). The latter factor justifies the application of the finite field method

in the study of the spectra of saturated hydrocarbons and certain other compounds without conjugated bonds and having absorption bands only in the far ultraviolet.

The variational method, which can be regarded as an alternative to the method of perturbation theory, makes it possible, at least under conditions remote from resonance, when $\nu \ll \nu_e$, to calculate the molecular dynamic electronic polarisability tensor without evaluating the contribution of each excited state[119,120]. Some information about these states is then introduced in the form of the wave functions of the singly and doubly excited configurations.

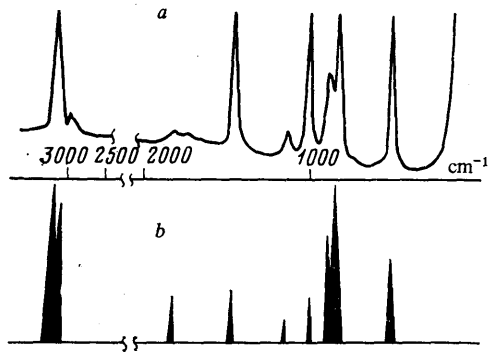


Figure 2. Raman spectra of cyclopropenone: *a*) experiment; *b*) calculation by the CNDO/2 method[105].

Within the framework of the method indicated, the sums of the first and second components of the binomial terms in Eqn.(8) are calculated by the variational procedure. Thus, in order to find the $\sigma\sigma$ component, the following expression is minimised in the first place at a specified frequency ν:

$$B_{\sigma\sigma}(Q, \nu) = \langle f|H - E_0 - h\nu|f\rangle + 2\langle\psi_0|\mu_\sigma|f\rangle, \qquad (9)$$

where f is the function to be varied, which is sought in the form of a linear combination of the wave functions of all the singly excited configurations, μ_σ the σ component of the dipole moment operator, H the electronic Hamiltonian, and E_0 and Ψ_0 are the energy and electronic wave function of the ground state, which are found by the usual quantum-chemical methods. At the minimum $f = f_0$ and $B_{\sigma\sigma}(Q, \nu)$ is close to the sum in Eqn.(8) being sought. Next the expression

$$\langle g|H - E_0|g\rangle + 2\langle g|\mu_\sigma|f_0\rangle, \qquad (10)$$

is minimised and g_0 for the function g being varied is found in the form of a linear combination of doubly excited configurations. Then

$$\frac{1}{h}\sum_e \frac{M_\sigma^{0e} M_\sigma^{e0}}{\nu_e - \nu} = B_{\sigma\sigma}(Q,\nu) + 2\langle g_0|H - E_0|\varphi_0\rangle, \qquad (11)$$

where $B_{\sigma\sigma}(Q, \nu)$ is calculated by Eqn.(9) with $f = f_0$.

Similar calculations (in each case for several values of the coordinate Q) by the CNDO/2 method enabled Svendsen and Tangaa[121] to calculate the first and second derivatives of the polarisabilities of methane, ethane, ethylene, and acetylene. An entirely satisfactory accuracy was achieved and the second order correction determined by Eqn.(10) proved to be small (≤10–20%). In addition, data were obtained for ethylene at several exciting light frequencies ν, which indicate, in conformity with the conclusions of the semiclassical theory, a faster increase of the intensity of the overtone with increase of ν; however, in the region of the resonance the calculations are merely conventional.

Selective allowance for the excited configurations in terms of the symmetry type led the authors[121] to estimates of the contributions of σ and π electrons; according to these estimates, the latter determine the polarisability of the ethylene molecule to the extent of 2/3, the derivative with respect to the symmetry coordinate of C–H to the extent of 12%, and the derivative with respect to the C=C coordinate to the extent of 95%.

The Raman line intensity corresponding to the vibrational transition $0 \to f$ is proportional to $\sum_{\rho\sigma} |(\alpha_{\rho\sigma})_{0f}|^2$ according to the quantum theory, where $(\alpha_{\rho\sigma})_{0f}$ is the Cartesian component of the electronic polarisability tensor.

When account is taken of the contributions of the sublevels ev, one can write the following equality for each tensor component:

$$(\alpha_{\rho\sigma})_{0f} = \text{const} \sum_{ev} \left[\frac{\langle 0|M_\rho^{0e}|v\rangle\langle v|M_\rho^{e0}|f\rangle}{\nu_{ev} - \nu} + \frac{\langle 0|M_\sigma^{e}|v\rangle\langle v|M_\rho^{e0}|f\rangle}{\nu_{ev} + \nu} \right], \qquad (12)$$

where 0, ν, and f are the quantum numbers of the vibrational sublevels of the ground, intermediate, and final states, M_σ^{0e} and M_ρ^{0e} are the Cartesian components of the vector of the dipole moment of the electronic transition $0 \to e$, ν_{ev} the frequency of the $00 \to ev$ transition, and ν the frequency of the incident light, which generally speaking should occur in a region far from or close to resonance with the frequency ν_{ev}. M_σ^{0e} and M_ρ^{0e} are usually regarded as functions of Q; the use of corrected quantities of the type of M^{0ev} is an alternative.

If there are many effective intermediate levels ev, it is more convenient to replace Eqn.(12) by the evaluation of the integral $\langle 00|G|0f\rangle$, where G is a Green function in which the functions Ψ_e and summation with respect to ev are used; thus one carries out initially the summation and then integration with respect to the coordinates of the electrons and nuclei[122].

The relation between the quantum and simple classical theories as regards the non-resonance Raman lines of the fundamental band can be determined by the direct proportionality between the matrix element $(\alpha_{\sigma\sigma})_{01}$ and the derivative $\partial\alpha_{\sigma\sigma}(Q)/\partial Q$. In certain investigations (including those quoted above[113,114]) the quantity $(\alpha_{\rho\sigma})_{0f}$ is set equal to the sum of the contributions of the derivatives of the polarisability with respect to all the normal coordinates Q (or the sum of the corresponding matrix elements of the polarisability), which, however, lacks any justification.

It is noteworthy that in a more sophisticated version of the classical theory the polarisability is not a single-valued function of Q and is replaced by the more general transmission function $\mathcal{K}(\nu, t)$, where t is the time; the latter includes an expression similar to Eqn.(12) with the corresponding decay constants[123].

Eqn.(12) describes the response of a system in a fixed initial position i. If a statistical description of a mixed *ensemble* of molecules and of its time variation is required, one can go over to the use of the density matrix ρ. The intensity of the secondary emission is then proportional to $\sum_i \rho_{ii} |\alpha_{if}|^2$, where the square of the modulus is averaged with respect to the *ensemble*.

The matrix elements $(\alpha_{\rho\sigma})_{0f}$ are calculated in the same way as in the calculation of the vibrational structure of the electronic transition $00 \rightarrow ev$ (see Section VIII) and requires information about the frequencies and modes of the atomic vibrations and the molecular geometry for the ground and all the excited states. The determination of these parameters is very laborious and is virtually impossible for complex molecules. For resonance Raman excitation, the treatment may be restricted to the contribution of a single electronic level e in Eqn.(12), but decay constants must be introduced.

If the linear term of the expansion of Ψ_e in series in terms of powers of Q by the Herzberg–Teller method is used for the calculation of the matrix elements $\langle 0|M^{0e}(Q)|v\rangle$ in Eqn.(12) or of M^{0e} in Eqn.(8), then we go over to the vibronic theory of Tang and Albrecht[102]. Specific calculations have not been made by Eqn.(12) within the framework of this theory and calculations by Eqn.(8) have already been described above.

The intensity of the Raman lines and the excitation spectra of these lines in the pre-resonance and resonance regions for butadiene and certain polyenes have been calculated[124] by Eqn.(12) but with allowance for only one first excited state π, π_1^*. In order to reduce the amount of computer time, the authors[124] used the approximate combined method proposed by Warshel and Karplus (see Section II) and obtained good results. They concluded that in the region of resonance the dominant Raman mechanism involves a process which, in terms of the semiclassical theory, is referred to as the modulation of the electronic transition frequency and is determined by the derivatives of ν_e.

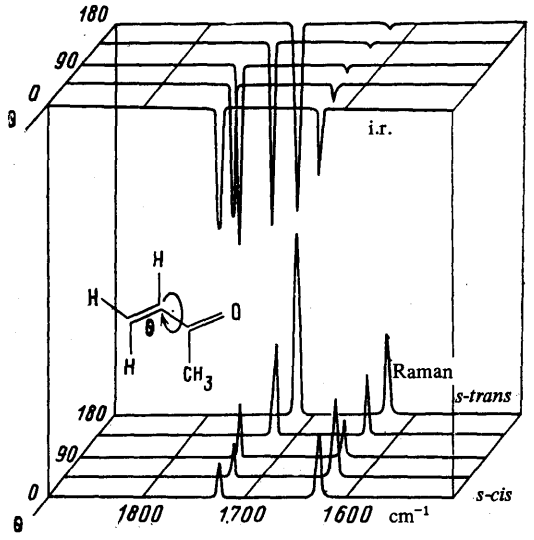


Figure 3. The line intensities associated with the stretching vibrations of the C=C and C=O bonds in the infrared and Raman spectra of methyl vinyl ketone, calculated by the CNDO/2 method[129] as a function of the angle θ of internal rotation about the central C–C bond.

The changes in the intensities of the Raman and infrared lines as well as the spectroscopic features of the conjugation of the C=C and C=O double bonds with a smooth variation of the angle of rotation θ about the C–C bond have been calculated[129] by the CNDO/2 method; the results are presented in Fig.3 (taking into account the data of other workers). The susceptibility of systems with any specified angle θ to calculation greatly extends the scope of the experiments. Other examples of calculations of the intensity have also been published[130–134].

The data presented above demonstrate the wide variety of methods used to calculate the Raman line intensities. Comparison of the results for ethylene obtained by different procedures (Table 7) shows that in most cases a satisfactory agreement with experiment was achieved; discrepancies with experiment by a factor of 2–4 have been noted for individual lines, but this accuracy is sufficient for the qualitative analysis of experimental data. In comparisons of this kind, one should bear in mind that the results of the calculation may vary by a factor of 2–3 owing to the inaccuracy of the atomic vibrational modes on which they are based.

Table 7. The relative Raman line intensities for ethylene on excitation under conditions remote from resonance in the visible region.

Type of vibration	ν̃, cm⁻¹	Finite perturbation theory with Φ obtained by different methods			Calculation of the partition function with respect to all excited states with Φ obtained by different methods			Vibronic theory	Experiment
		CNDO/2 (Ref.106)	non-emp. (Ref.116)*	CNDO/2 (Ref.128)	CNDO/2 (Ref.114)	CNDO/S (Ref.109)	non-emp. (Ref.26)**	CNDO/2 (Ref.114)	
A_{1g}	3026	1	1	1	1	1	1	1	1
A_{1g}	1630	0.1	0.24	0.2	0.12	0.30	0.18	0.53	0.30
A_{1g}	1342	1.36	1.35	1.65	1.04	0.60	0.46	0.62	0.53
B_{1g}	3103	0.59	0.92	0.98	0.57	0.97	0.38	0	0.2
B_{1g}	1220	0.03	0	0	0	0.01	0	0	0

*Non-empirical calculation in terms of a biexponential basis set with polarising functions.

**Non-empirical calculation in terms of the OST-4-31G basis set.

X. CONCLUSION

The susceptibility of the electronic wave functions and of the energy of excited molecules to calculation in terms of LCAO schemes permits the invocation of molecular orbital methods in the study of virtualiy any molecular-orbital phenomena; among them, one can note also those which have begun to be investigated only in recent years, for example, the Raman-induced Kerr effect, the Raman-optical activity, simultaneous electronic (or vibrational) transitions in components of the mixture, the beats in the secondary emission of light by molecules associated with the interference of electronic states, non-linear optical phenomena, the manifestation of the anharmonic interaction of the modes and of non-adiabatic conditions, etc.

In principle, one can predict the overall form (and interpret) the absorption and emission spectra of simple molecules, complexes, ions, radicals, and molecular crystals and to infer the dependence of the spectra on the conformation, on the initial electronic state, or on additional perturbations. At the same time it is possible to refine and supplement the available information about the force field, to determine the signs of the derivatives of the polarisability and the dipole moment, to estimate

the frequencies of the unobserved transitions, to characterise the potential energy curves for excited states, etc.

The accuracy of the calculations of the spectral parameters is at present much lower than the experimental accuracy but is sufficient for the solution of many spectrochemical problems; the combination of calculated and experimental data leads to a more complete and reliable description of the spectrum.

The use of quantum-chemical methods makes it possible to increase the amount of information derivable from spectroscopic studies, to discover the principles underlying the empirical relations between the spectra and various physical and chemical properties of molecules, and to elucidate the nature of the interaction between the atomic groups in complex molecules on the basis of the idea of the interaction of electrons and nuclei.

Further advances in the application of quantum-chemical methods to spectroscopy will be evidently closely related to progress in computer techniques. The development of fast computers will extend the scope for taking into account more fully the electron correlation (particularly as a result of the inclusion of highly excited configurations in the SCF method) and will permit the abandonment of many simplifications, for example,the appreciable limitation of the size of sets of basis functions and the neglect of the contributions of the *d* and *f* atomic orbitals of the elements in the first two Periods, the empirical selection of certain parameters, the restriction to models simulating a small fragment (for example, an active centre) of a complex molecule, etc. On the other hand, one can count on considerable progress in the study of molecular systems and processes as a function of time.

It is noteworthy that compounds both with and without heavy atoms are being successfully studied in experimental spectrochemistry. The compounds with heavy atoms are not susceptible to investigation by the majority of quantum-chemical methods. The accumulation of experience in the parametrisation of such systems will undoubtedly diminish the gap between the scopes of the experimental and theoretical methods. At the same time, one may expect further successes in the development of ways of taking into account relativistic effects, which in certain systems can appreciably alter the disposition of electronic levels, the transition probabilities, and the frequencies ω; the influence of these effects increases very rapidly with increase of the effective nuclear charge and can therefore prove comparable to, for example, the result of the Coulombic interaction and can be much greater than the influence of the usual conjugation of double bonds.

Progress in the development of computational methods is closely related to the endeavour to develop more universal and more accurate but sufficiently compact versions and, on the other hand, to limit the elements of subjectivity and uncertainty, which are expressed, for example, in the selection of a variant of the computational method leading to the best result in the solution of a specific problem, in the adaptation of parameters, and in the introduction of corrections specific to a particular type. As a result of these features, the application of even non-empirical methods proved to be far from free from empirical characteristics.

The alternatives to the LCAO approximation, which resemble the usual schemes as regards their conventional aspect, are of great interest, but hitherto fairly modest advances have been made on these lines, being limited by the imperfection of the proposed schemes and the large amount of computer time required.

Bearing in mind all the data described here, one can say in conclusion that the combination of the methods of experimental spectroscopy and quantum chemistry will greatly increase the effectiveness of the studies of molecular structures and the mechanisms of chemical processes and will extend the scope of practical chemical applications of spectroscopy.

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Enzyme Catalysis in Organic Synthesis

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The present state of enzyme catalysis and the prospects for its introduction in organic synthesis are examined. The physicochemical approaches whereby the yield of the desired product can be increased under conditions favourable for biocatalysis (at the optimum of the catalytic activity and stability of the enzyme) are analysed. Together with classical equilibrium and kinetic preparative methods, the thermodynamic features and general methodological aspects of a new approach—enzymatic synthesis in two-phase systems comprising water and a water-immiscible organic solvent—are discussed in detail.
The bibliography includes 170 references.

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I. INTRODUCTION

The application of biological catalysts (enzymes) in organic synthesis appears to be extremely promising and in many instances has a number of significant advantages over the classical methods of synthetic chemistry. This is due primarily to the fact that enzymes exhibit a unique specificity (selectivity), i.e. the reactions which they catalyse proceed as a rule via a single pathway without side processes. Furthermore, the unsurpassed catalytic activity of enzymes ensures synthesis under mild conditions. Consequently the practical application of biocatalysis might result in the saving of energy and resources and in addition might decrease the damage caused by modern chemical technology to the environment.

Despite the evident advantages of enzyme catalysis, the decisive steps in this field were outlined only the last 10–15 years. This is due, firstly, to the general progress in the study of the properties, structure, and functions of enzymes (see, for example, Refs.1–4), and, secondly, to the introduction of immobilised enzymes[5,6]. As a result of immobilisation (for example, the covalent attachment of the enzyme to a water-insoluble particle, the encapsulation of the enzyme in a gel, and the adsorption of the enzyme on a carrier), it is possible to separate the heterogeneous catalyst from the reaction medium and to use it again. Furthermore, immobilisation constitutes a method of the specific modification (improvement) of practically important properties of enzymes[5-7] and in the first place of their stability[8-11]. Thirdly and finally, enzymes have become available in large amounts in connection with the development of methods for their microbiological synthesis and isolation[12,13].

The successes achieved using biocatalysis in preparative organic synthesis as well as the likely prospects for their applications have been discussed in a number of reviews[5,6,14-27]. The vast majority of enzymatic processes have been developed only on a laboratory scale: typical examples are presented in two publications by the authors of this review[8,9]. However, certain processes have already been applied on an industrial scale[14,15].

Nevertheless there exists one factor which limits the application of enzymes in preparative organic synthesis on a wider scale. The point is that enzymes retain their unique catalytic properties only over a fairly narrow range of conditions, at neutral or nearly neutral pH and at not unduly high temperatures. However, the equilibria in many reactions of practical importance are displaced towards the initial reactants under these conditions. In other words, when biocatalysis is employed, a situation frequently arises where the conditions necessary for the retention of the catalytic properties of the enzyme are incompatible with the optimum thermodynamic conditions for the attainment of a high yield in the catalysed reaction.

The conflict between the relatively "severe" conditions under which the chemical reaction should take place and the "fragile" nature of the biocatalyst (its relatively labile structure) can be resolved in principle. One of the ways involves the stabilisation of the enzyme in relation to the inactivating influences of increased temperature, extreme pH values, organic solvents, etc. Significant advances have already been made on these lines[8-11] and the relevant studies are being continued (see, for example, Martinek et al.[16]). It is to be hoped therefore that in the future the classical approaches of preparative organic synthesis (alteration of temperature and pH, selection of reaction medium) will become common also in enzymatic reactions. This review deals with fundamentally different solutions of the given problem, namely physicochemical approaches which make it possible to increase the yield of the desired product without the stabilisation of the enzyme, directly under conditions favourably for biocatalysis.

II. EQUILIBRIUM APPROACHES

The approaches whereby the yield of the desired product (in enzyme-catalysed thermodynamically unfavourable synthetic reactions) can be improved by a shift of the chemical equilibrium will be referred to as equilibrium approaches.

1. The Method Based on the Low Solubility of the Product

The shift of the chemical equilibrium in a favourable direction may be caused by the poor solubility in water of one or several final products (under the reaction conditions), which

precipitate. The physicochemical essence of this phenomenon will be considered in relation to the reaction

$$A + B \rightleftharpoons C\downarrow (ppt). \quad (1)$$

The effective equilibrium constant $K_{eff} = [C]_{soln} + [C]_{ppt}/[A][B]$ is

$$K_{eff} = \frac{K}{[C]_{soln}} \left\{ [A]_0 (K/[C]_{soln})^{1/2} - 1 \right\}, \quad (2)$$

provided that the true equilibrium constant (in the absence of the precipitate) is given by $K = [C]/[A][B]$ and the material balance equation is of the form $[A]_0 = [A] + [C]_{soln} + [C]_{ppt}$ for $[A]_0 = [B]_0$, where $[A]_0$ and $[B]_0$ are the initial concentrations of the initial reactants, [A], [B], and [C] are the equilibrium concentrations of the reactants in solution, $[C]_{soln}$ is the maximum concentration of the dissolved product (solubility), and $[C]_{ppt}$ the concentration of the precipitated reactant (referred to the volume of the entire system). Eqn.(2) is valid only in the presence of a precipitate, i.e. for $[A]_0 > [C]_{soln} + [A] = [C]_{soln} + \{[C]_{soln}/K\}^{1/2}$.

It follows from Eqn.(2) that the shift of equilibrium(1) observed when the product precipitates should be more pronounced at high concentrations of the initial reactant and naturally for a lower solubility of the final product.

Applications. The method described is usually employed for the synthesis of the amide (peptide) linkage via the general mechanism

$$R_1COO^- + R_2NH_3^+ \rightleftharpoons R_1CONHR_2 + H_2O.$$

In this reaction the solubility of the product is as a rule significantly lower than those of the initial reactants because two charges disappear during the synthesis (see, for example, the synthesis of anilides[28-31], aminoacid phenylhydrazides[30,32,33], and oligopeptides with a specified sequence[29,30,34-43]). Various proteolytic enzymes are used as catalysts in this instance: α-chymotrypsin, trypsin (see, for example, Isowa et al.[38]), bacterial metalloproteinases[40], papain[43], etc.

Limitations of the method. The method suffers from two significant disadvantages. Firstly, the requirement for a low solubility of the final product greatly limits the choice of compounds which can be synthesised in this way[37]. In order to ensure a sufficiently low solubility of the corresponding product, sometimes the ionogenic groups in the initial reactants must be protected[36,43]. Secondly, the formation of the precipitate in the reaction hinders the application of water-insoluble enzyme derivatives as catalysts.

2. The Application of Consecutive Reactions

The yield of the reaction increases if one of the products is involved in a consecutive (enzymatic or non-enzymatic) thermodynamically favourable reaction, for example:

$$A + B \overset{K}{\rightleftharpoons} C + D, \quad (3)$$

$$D \overset{K_T}{\rightleftharpoons} F. \quad (4)$$

Since reaction (4), additionally introduced into the system, must be thermodynamically favourable, i.e. the condition $\Delta G_T < 0$ must hold, the equilibrium constant of the overall reaction $A + B \rightleftharpoons C + F$ must be greater than the equilibrium constant of the initial synthetic reaction (3):

$$K_\Sigma = \exp\left(-\frac{\Delta G^0 + \Delta G_T^0}{RT}\right) > K = \exp\left(-\frac{\Delta G^0}{RT}\right). \quad (5)$$

Reactions with formation of inorganic pyrophosphate. This method proved to be particularly fruitful in relation to reactions of the type

$$A + B \rightleftharpoons C + PP_i,$$

where PP_i is the organic pyrophosphate. Subsequent hydrolysis of the pyrophosphate, catalysed by the addition of inorganic pyrophosphatase added to the system (II),

$$PP_i \overset{II+H_2O}{\rightleftharpoons} 2P_i, \quad (6)$$

is a thermodynamically very favourable reaction; for example, at pH 7 the free energy of reaction (6) is $\Delta G_T^\circ = -5.27$ kcal mol^{-1}.[44] This ensures a significant shift of the equilibrium of the overall reaction towards the products. For example, in the synthesis of the nucleotide orotidine 5′-monophosphate (OMP) from orotic acid (OA) and 5-phospho-α-D-ribosyl diphosphate (PRPP),

$$OA + PRPP \rightleftharpoons OMP + PP_i, \quad (7)$$

catalysed by phosphoribosyltransferase, it was possible[45] to raise the yield from 54 to 100% by the introduction of the additional process (6). This method, based on the removal of the pyrophosphate side product, has been used in the enzymatic synthesis of NAD,[46] labelled galactoses[47], nucleic acids[48], and β-UDP-acetylglucosamine[49].

Regeneration of the cofactor of the enzymatic reaction. Many enzymatic reactions proceed with participation of cofactors:

$$A + Cof \overset{enzyme}{\rightleftharpoons} B + Cof', \quad (8)$$

where Cof and Cof′ are the initial and "spent" forms of the cofactor respectively[50,51]. The consumption of the cofactor greatly increases the cost of the products and ultimately restricts the wide-scale application of enzymes in organic synthesis. In recent years much effort has therefore been directed to the creation of the so-called cofactor regeneration systems. The regeneration usually takes place as a result of a coupled enzymatic or non-enzymatic reaction (or set of reactions) of the type

$$C + Cof' \rightleftharpoons D + Cof \quad (9)$$

(see the relevant reviews[6,9]). Consequently, in the regeneration of the cofactor, the yield of the product B may be determined by the equilibrium of the overall reaction $A + C \rightleftharpoons B + D$. This has been shown clearly[52] for the modification of steroids:

$$\text{steroid} + NAD \overset{K=2.6\cdot10^{-8}}{\rightleftharpoons} \text{steroid} + NADH, \quad (10)$$

(the steroid fragments are CH–OH and C=O, respectively)

catalysed by 20β-hydroxysteroid dehydrogenase.

The regeneration of the cofactor

$$NADH + \text{pyruvate} \overset{K_T=3.8\cdot10^{11}}{\rightleftharpoons} NAD + \text{lactate}, \quad (11)$$

catalysed by lactate dehydrogenase, is a thermodynamically favourable process. This is why the equilibrium of the overall process (10)–(11) is displaced towards the formation of the product, namely the keto-form of the steroid: $K_\Sigma = KK_T \approx 10^4$.

Other examples. In an analogous system with regeneration of the cofactor

$$\text{steroid} + NADH \xrightarrow{\text{20β-hydroxysteroid dehydrogenase}}$$

(steroid fragment C=O)

$$\rightarrow \text{steroid} + \text{NAD}, \quad (12)$$

$$\text{NAD} + C_2H_5OH \xrightarrow{\text{alcohol dehydrogenase}} \text{NADH} + CH_3CHO, \quad (13)$$

it was found[58] that the overall equilibrium constant is approximately unity. In order to shift the equilibrium towards the formation of the hydroxy-form of the steroid, the familiar reaction involving the strong binding of the acetaldehyde formed as a side product into the semicarbazone was used:

$$CH_3CHO + NH_2NHCONH_2 \rightleftharpoons CH_3CHNNHCONH_2 + H_2O. \quad (14)$$

Thus the additional process accompanying the synthetic reaction and responsible for the shift of the overall equilibrium to the right may be both an *enzymatic* reaction of type (6) and a *non-enzymatic* chemical reaction, for example reaction (14). In principle, this thermodynamically favourable auxiliary process can be also physical. Thus Laskowski and coworkers[54] observed the trypsin-catalysed synthesis of the peptide linkage in the active centre of the soyabean trypsin inhibitor:

$$-^{64}\text{Lys} + {}^{65}\text{Ile} \rightleftharpoons -^{64}\text{Lys}-^{65}\text{Ile} + H_2O. \quad (15)$$

The equilibrium of the synthetic reaction is displaced to the right, because the product forms a stable complex (binding constant approximately 10^8) with trypsin.

3. Enzymatic Synthesis in Water–Organic Solvent Mixtures

The synthesis of compounds such as ethers, esters, amides, and anhydrides, etc. is usually carried out by the reversal of hydrolytic reactions, so that water is one of the products:

$$A + B \overset{K}{\rightleftharpoons} C + H_2O. \quad (16)$$

Under the conditions of the enzymatic reaction (in water), the equilibria of such reactions are therefore as a rule displaced to the left as a consequence of the high concentration of the aqueous component (55.5 M).

Physicochemical (sources) of the shift of the equilibrium. Evidently the yield of the product C can be increased by reducing the concentration of water in the system, because $[C] = K[A][B]/[H_2O]$. For this purpose, it is convenient to carry out the reaction not in water but in a water–organic solvent mixture with a high content of the non-aqueous component: dimethyl sulphoxide, formamide, dimethylformamide, dioxan, acetone, ethylene glycol, glycerol, monohydric alcohols, etc. (see the relevant reviews[9,11,55]).

Together with this trivial "concentration" effect, equilibrium (16) is influenced also by factors associated with the medium, such as the change in the dielectric constant or polarity, etc. Among specific effects of this kind, the shift of the equilibrium caused by the change in the pK of the acids (and/or) bases involved in the reaction must be regarded as extremely common.

We shall consider this phenomenon in relation to the synthesis of the amide linkage:

$$\begin{array}{ccccc} R_1COOH & + & R_2NH_2 & \rightleftharpoons & R_1CONHR_2 + H_2O. \\ \downarrow\uparrow K_a & & \downarrow\uparrow K_b & & \\ R_1COO^- & & R_2NH_2^+ & & \end{array} \quad (17)$$

In water (at any pH) the equilibrium in this reaction is displaced to the left primarily due to thermodynamically favourable ionisation processes involving at least one of the initial reactants. On passing to a water–organic solvent mixture with a high content of the non-aqueous component steady shifts of the observed pK_a and pK_b take place due to both electrostatic and solvation effects[56]. As a rule the pK_a for the acid changes most significantly: it increases, i.e. the ionisation equilibrium shifts towards the uncharged form. As a result, the equilibrium of the entire reaction (17) is displaced towards the product being synthesised[57,58]. For example, on passing from water to an 85% solution of butane-1,4-diol, the equilibrium constant for the synthesis of the peptide linkage increased by a factor of 80.[57]

The systems investigated. Water–organic solvent mixtures with a high content of the non-aqueous component have been used to synthesise the ethyl and glyceryl esters of *N*-acetyl-L-tyrosine[59], urea[60], glycerophosphate[61], aliphatic acid esters[62,63], dipeptides[57,64], and human insulin[64,65], as well as for the resynthesis of the hydrolysed peptide linkage in ribonuclease[58]. An unsuccessful attempt has also been made to synthesise sucrose from glucose and fructose[66].

Limitations of the method. A significant disadvantage of the method is that, in the presence of high concentrations of organic solvents, an appreciable impairment of important characteristics of enzymes such as catalytic activity, specificity, and stability is as a rule observed (see paper of Klibanov et al.[61] and the references therein as well as Butler's review[55]). Frequent attempts have therefore been made to protect the enzyme from inactivation by organic solvents via immobilisation (see the discussion in the papers by Martinek and coworkers[67,68]). However, this approach has still not let to sufficiently stable enzyme preparations. For this reason, investigators usually select simply by trial and error conditions (organic solvent and its concentration) such that the shift of the equilibrium towards synthesis is sufficient and at the same time an appreciable inactivation of the enzyme is not observed.

In contrast to these empirical approaches, a criterion, based on scientific principles, has been recently formulated[61] for the selection of the organic solvent as the component of the medium in enzymatic (including synthetic) reactions. Nevertheless, even under optimum conditions, it is not possible to reduce the concentration of water in the system by a factor greater than 10–20, which naturally restricts the scope of the method.

Criterion for the selection of the optimum solvent (from the standpoint of its influence on the enzyme). Such a criterion can be justified on the basis of general ideas concerning the relative role of the forces maintaining the native structure of the protein molecules in aqueous solutions: "hydrophobic interactions" play a dominant role[69,70] (despite recent doubts[71,72]). Consequently, a "good" solvent for the protein should not affect such interactions.

In order to answer the question which solvents have this property, we turned[61] to the results obtained for the information of micelles by surfactants in various solvents. Thus Ray[73] concluded that hydrophobic interactions constitute merely a special case of solvophobic interactions.

In terms of their capacity to undergo solvophobic interactions, all solvents can be divided into three classes: the first class includes water, glycerol, ethylene glycol, aminoethanol, formamide and certain others, the second class includes methylformamide and dimethylformamide, and the third includes methanol, ethanol, and toluene. Solvophobic interaction occur to the greatest extent in the solvents belonging to the first class (thus detergent micelles are formed only in these solvents); they are manifested much less in the solvents of the second class and are virtually

absent in solvents of the third class. According to Ray[73], this difference is caused by the fact that solvents of the first class contain in their molecules at least two or three fragments capable of forming hydrogen bonds. As a result of intermolecular interactions, hydrogen bonds give rise to rigid (thermodynamically unfavourable) skeletal solvent structures around the solvophobic solute molecules. This leads to solvophobic (or, in the special case of water, hydrophobic) interactions. In a series of solvents of the first class solvophobic interactions occur most effectively (this has been inferred from the critical micelle-formation concentrations) in water and glycerol; in the remaining solvents this capacity is significantly smaller.

These data enabled us to formulate[61] a criterion for the selection of the optimum solvent. The criterion is universal, because the effectiveness of solvophobic as well as hydrophobic[74] interactions is not determined by the nature of the interacting molecules but depends primarily on the nature of the solvent. Consequently, if it is assumed that the main role in the maintainence of the structure of the protein molecules is that of hydrophobic interactions, one must recognise that the best solvents for enzymatic reactions must be those of the first class and among them water (which is used in nature) and glycerol. In this connection it is appropriate to mention that in certain studies it has indeed been found experimentally that solvents of the first class, particularly glycerol and to a lesser extent ethylene glycol, denature proteins to a much lesser extent than others. This empirical finding has found a physicochemical explanation[61,73].

In order to confirm the above views, we investigated[61,75] the dependence of the catalytic activities of certain enzymes (acid phosphatase, α-chymotrypsin, formate dehydrogenase, and penicillin amidase) on concentration in aqueous solutions of certain organic solvents. It was found[61,75] that glycerol and ethylene glycol (which belong to the first class) inactivate enzymes to a lesser extent than dimethylformamide (second class) or ethanol (third class). The same conclusion follows from a comparative study carried out recently by Butler[55] on acid phosphatase in aqueous solutions of ethylene glycol (first class) and methanol (third class). These facts are in good agreement with the concept developed by ourselves[61], according to which the native structure of protein molecules (and hence their catalytic activity) are maintained in those solvents which are capable of solvophobic interactions. At the same time one should note that the three-dimensional structure of protein molecules is maintained not only by hydrophobic interactions but also by other types of bonding—electrostatic or hydrogen, etc.[69]; therefore the replacement of water by another solvent cannot be totally "ignored" by the protein. This also probably explains the decrease of the catalytic activity at an unduly high glycerol concentration[61,75] (see also the discussion of the criteria for the selection of the solvent in Butler's review[55]). Nevertheless, in many instances water–glycerol mixtures (or mixtures of water and a solvent of the first class) are entirely suitable as media for synthetic reactions[59,61,76–82]. We shall consider one example.

Enzymatic synthesis of glycerophosphate. In water (at pH 5) the equilibrium constant "does not favour" the synthesis of glycerophosphate[83]. For example, at glycerol and inorganic phosphate concentrations of 2 mM the yield of glycerophosphate should be approximately only 0.01%. The situation is different in 95% glycerol. Fig.1 (curve 3) illustrates the kinetics of the accumulation of glycerophosphate in its enzymatic synthesis from glycerol and phosphate[61]. The same level of glycerophosphate in the system can be reached also in the solvolysis of α-glycerophosphate (curve 1) or β-glycerophosphate (curve 2) by acid phosphatase, which shows that the level of accumulation of glycerophosphate attained corresponds to true thermodynamic equilibrium in the system and is not limited, for example, by the inactivation of the enzyme in the water–organic solvent mixture. Fig.1 shows that the yield of glycerophosphate in 95% glycerol is approximately 35%, which is entirely acceptable for preparative purposes.

III. NON-EQUILIBRIUM (KINETIC) APPROACHES

In certain cases it is possible to attain a concentration of the desired product so high that it does not correspond to the thermodynamic state of the system and arises and persists for a specific time as a result of purely kinetic factors. This approach is widely used to increase the yield of products in enzyme-catalysed thermodynamically unfavourable synthetic reactions.

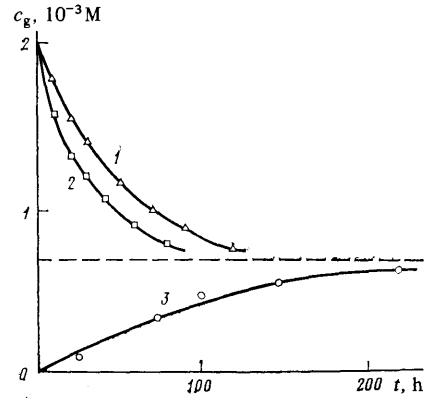


Figure 1. Kinetic curves for the acid phosphatase-catalysed hydrolysis (curves *1* and *2*) and synthesis (curve *3*) of glycerophosphate in 95% glycerol (c_g = glycerophosphate concentration): 1) α-glycerophosphate; 2) β-glycerophosphate. The dashed line represents the equilibrium glycerophosphate concentration[61].

1. Transfer Reactions Catalysed by Hydrolytic Enzymes

If the equilibrium in the reaction

$$\text{Acyl—OH} + \text{Nucl—H} \rightleftharpoons \text{Acyl—Nucl} + \text{H}_2\text{O}$$

is displaced towards the initial reactants, the yield of the product Acyl–Nucl can be increased significantly with the aid of the kinetic procedure described above.

The essential physicochemical nature of the method. For example, suppose that it is necessary to synthesise a derivative Acyl–X, which, together with the inevitable hydrolysis, can interact effectively with a nucleophile (Nucl–H):

$$\begin{array}{l} \text{Acyl—X} \xrightarrow{\text{H}_2\text{O}} \text{Acyl—OH} + \text{HX}, \\ \quad -\text{XH}\downarrow\ +\text{Nucl—H} \\ \text{Acyl—Nucl} \xrightarrow{\text{H}_2\text{O}} \text{Acyl—OH} + \text{Nucl—H}. \end{array} \qquad (18)$$

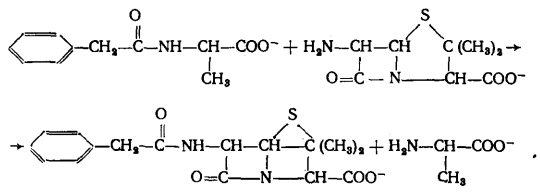
The desired product Acyl–Nucl will then be formed in the reaction mixture as an intermediate, which subsequently hydrolyses. Evidently the time variation of the concentration of the intermediate Acyl–Nucl should be represented by a curve with a maximum (see the kinetics of consecutive reactions[84]). It is important that, for certain ratios of the concentrations of the reactants and the rate constants for the individual stages, the maximum concentration of Acyl–Nucl may prove to be significantly higher than the equilibrium value.

We shall consider reaction (18) in greater detail under catalytic conditions (with participation of a hydrolase). The mechanism of catalysis by many enzymes of the class of hydrolases includes the formation of an intermediate covalent compound comprising the acyl component of the substrate and the enzyme—the acylenzyme[3,85]. In subsequent stages the acylenzyme decomposes under the influence of water with regeneration of the catalytically active enzyme (E) and the formation of the corresponding acid [stages (I) and (II)]:

$$\begin{array}{l} \text{Acyl–X} \xrightarrow[-\text{X}]{\text{E; (I)}} \text{Acyl–E} \xrightarrow[-\text{E}]{\text{H}_2\text{O; (II)}} \text{Acyl–OH} \\ \qquad\qquad -\text{E}\downarrow\ (\text{III})\ \uparrow +\text{Nucl} \qquad\qquad \text{H}_2\text{O}\uparrow\ (\text{V})\ \downarrow -\text{E} \\ \text{Acyl–Nucl} \xrightarrow[-\text{Nucl}]{\text{E; (IV)}} \text{Acyl–E} \end{array} \qquad (19)$$

However, when a nucleophile (Nucl), capable of competing effectively with water, is present in the system, there is a possibility of a parallel reaction [(I) and (III)] and the intermediate Acyl–Nucl will be formed in the reaction mixture and will be subsequently hydrolysed enzymatically in stages (IV) and (V).[3,86]

The kinetics of the accumulation and hydrolysis of the product Acyl–Nucl are described by a system of differential equations which cannot be solved in the general case in an analytical form and its solution requires the application of numerical integration methods on a computer. The kinetics of the enzymatic transfer of the acyl residue to the nucleophile have been investigated in very great detail[87,88]. Fig. 2 shows as an example how benzylpenicillin accumulates in the reaction mixture in its synthesis from phenylacetylglycine and 6-aminopenicillanic acid:



(20)

The reaction was catalysed[87] by penicillin amidase. Fig. 2 shows that the concentration of the product at the kinetic optimum greatly exceeds the equilibrium level (dashed line).

For the further development of the given kinetic method, it is important that the experimental results are fully described by the theoretical curve plotted using kinetic and equilibrium constants determined from independent experiments[87,88], which leads to the possibility of predicting the maximum yield and hence of optimising the synthetic process.

Application. Botvinnik and coworkers were some of the first investigators to apply the above method in the stereospecific synthesis of oligopeptides with a specific sequence (using α-chymotrypsin as the catalyst)[89,90]; later, the synthesis of peptides was investigated in detail by Japanese workers[91,92]. The method has also been used for the penicillin amidase-catalysed synthesis of β-lactam antibiotics[87,88,93], phosphatidylserine[94], and phosphatidylethanolamine[95] (using phospholipase as the catalyst).

Limitations of the method and prospects. The application of the method is limited by the fact that it is necessary to select (and synthesise) an initial substrate Acyl–X which is hydrolysed fairly slowly via the catalytic pathway (II) [see reaction (19)] and reacts vary effectively (rapidly) with the added nucleophile [stage (III)]. The maximum yield of the product Acyl–Nucl is also limited by its subsequent hydrolysis [stages (IV) and (V)]. In principle, both these hydrolytic "obstacles" to the given method can be at least partially suppressed by carrying out the synthesis under conditions ensuring the precipitation of the product[89–92]. In future investigations an attempt may be made to reduce the undesirable hydrolysis of the initial reactant Acyl–X and the product Acyl–Nucl by carrying out the synthesis in a water–organic solvent mixture, with a high content of the non-aqueous component, rather than in water. For the same purpose, to increase the kinetically controlled yield, the application of two-phase systems comprising water and a water-immiscible organic solvent can also prove useful (see below).

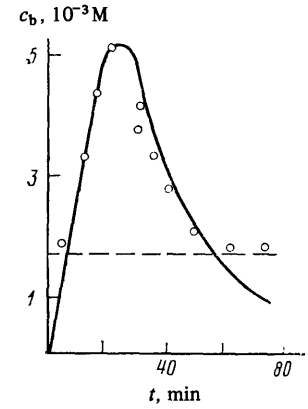


Figure 2. Kinetic curve for the accumulation of the product in the synthesis of benzylpenicillin (c_b = benzylpenicillin concentration) from phenylacetylglycine and 6-aminopenicillanic acid catalysed by penicillin amidase. Circles—experimental data; continuous curve—the result of the solution of a system of differential equations by numerical integration on a computer[87].

2. Kinetically Controlled Equilibrium

An extremely interesting phenomenon has been observed recently[96]: the hydrolysis of the ethyl ester of *N*-acetyl-L-tyrosine catalysed by α-chymotrypsin immobilised on charged carriers (Sephadexes) does not go to completion at pH 8 (only to the extent of 60–90% depending on the conditions). Furthermore, the synthesis of the ester from the corresponding acid and alcohol takes place under the same conditions (in water in the presence of an enzyme immobilised on a carrier):

$$\text{N–Acet–}L\text{-TyrOH} + \text{EtOH} \rightleftharpoons \text{N–Acet–}L\text{-TyrOEt} + \text{H}_2\text{O}$$

(Fig. 3). As a result, it is possible to attain the same composition of the reaction mixture both from the side of synthesis and from the side of hydrolysis. This limiting composition does not change for a long time. At the same time, the above

state of the system does not correspond to the true thermodynamic equilibrium. Thus, when a certain amount of free (non-immobilised) enzyme is added to the system, the concentration of the ester falls almost to zero.

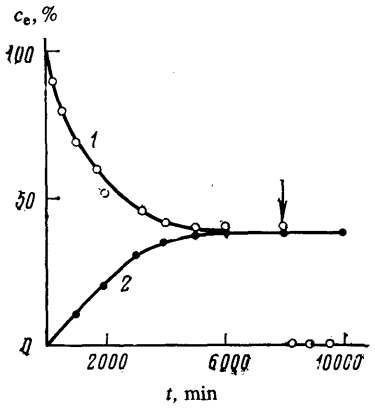


Figure 3. Kinetic curves for the hydrolysis (curve *1*) and synthesis (curve *2*) of the ethyl ester of *N*-acetyl-L-tyrosine (c_e = ester concentration) catalysed by α-chymotrypsin immobilised on charged carriers (sephadexes). The arrow denotes the instant of the addition of the non-immobilised enzyme[96].

It is believed[96] that the phenomenon is associated with the fact that the free energy of the chemical reaction changes in the electrical double layer (EDL) on the surface of the carrier (relative to the free energy of the same reaction in the absence of the electric field) due to the orientation energy of the reactant dipoles. Ultimately it may turn out that within the EDL the reaction equilibrium favours the synthesis of the product to a greater extent than in water. Naturally the volume of the EDL on the surface of the carrier constitutes only a fraction of the total volume of the system and the shift of the equilibrium in it should have a very insignificant effect on the overall equilibrium composition of the reactants throughout the entire system. However, if the rates of reaction in the bulk phase of the system are low compared with the corresponding rates in the EDL, i.e. if the reaction equilibrium in the entire system is established solely via the EDL, the observed equilibrium composition of the reactants may be kinetically controlled by the equilibrium of the reaction in the electrical double layer. This is why the authors[96] proposed the term "kinetically controlled equilibrium" for phenomena of this kind.

The kinetic control of the equilibrium can be achieved, for example, *catalytically* if the catalyst is incorporated within the EDL. In this case the rate of reaction within the EDL is naturally higher than in the bulk phase of the system and for this reason (if the equilibrium within the EDL favours synthesis) it is possible to achieve a fairly high yield of the product, which naturally does not correspond to equilibrium in the bulk phase of the entire system. This situation is believed[96] to occur precisely in the example discussed above.

From the same standpoint, it is apparently possible to explain also the finding that the hydrolysis of the same substrate (the ethyl ester of *N*-acetyl-L-tyrosine) takes place only to the extent of 60% when the reaction is catalysed by α-chymotrypsin immobilised on a spiropyran matrix[97]; the synthesis from the acid and alcohol takes place correspondingly to the extent of 40% (Fig.4). It is of interest to note that this effect occurs only under illumination; in the dark the synthetic reaction does not occur, while the hydrolysis proceeds to the extent of 100%. Fig.4 shows that, as a consequence of this, there is a possibility of regulating the position of the "kinetically controlled equilibrium" with light. Japanese workers explain this phenomenon by the fact that the properties of the matrix, which apparently determine the chemical reaction equilibrium near or within it, are different in the dark and in the light[97].

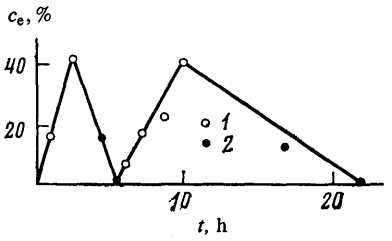


Figure 4. Kinetic curves for the synthesis (curve *1*) and hydrolysis (curve *2*) of the ethyl ester of *N*-acetyl-L-tyrosine catalysed by α-chymotrypsin immobilised on a spiropyran matrix: 1) illuminated system; 2) system in the dark[97].

Both systems were discovered quite recently (they were reported in 1978 and 1979 respectively), have been comparatively little investigated (the mechanism and reaction of the second system are still not entirely clear), and it is therefore difficult to assess their advantages and disadvantages and also the potential possibilities of their applications in enzymatic organic synthesis.

IV. ENZYMATIC SYNTHESIS IN TWO-PHASE SYSTEMS COMPRISING WATER AND A WATER-IMMISCIBLE ORGANIC SOLVENT

Each of the methods described above, which makes it possible to displace the equilibrium (or in the general case to increase the yield of the desired product) in enzyme-catalysed thermodynamically unfavourable synthetic reactions, is applicable in only a limited number of instances. An equilibrium approach has been proposed recently, which apparently constitutes a more general solution of the problem. Its essential feature is that the reaction is carried out in a two-phase system water–water-immiscible organic solvent[67,68]. The enzyme is present in the aqueous phase and it is therefore unnecessary to solve the traditional problem of stabilising the enzyme with respect to denaturation by the organic solvent. The added substrates, dissolved in the organic phase, diffuse from the latter into water, react chemically under the influence of the enzyme, and the products diffuse from water back to the organic phase. Thus, the thermodynamic equilibrium in the given reaction is established throughout the water–organic solvent system via water (with the aid of the enzyme present in water). The volume fraction of the organic phase can be in principle as close to unity as is necessary (the water content must be only sufficient to dissolve the required amount of the enzyme with retention of catalytic activity). Consequently the equilibrium conditions

in such a system can be as close as required to the equilibrium in the pure organic medium.

An enzymatic two-phase system can be created either in the form of two immiscible layers, or as an emulsion of an aqueous solution of the enzyme in the organic phase, or, finally, by the incorporation of the enzyme in the inverted micelles of the surfactant[16,98] (see also the relevant reviews[8-11]) or in liquid membranes[99]. However a suspension of particles (porous glass or ceramic, whole fibres, gel grains, microcapsules, etc.) impregnated with an aqueous solution of the enzyme is much more convenient for technological purposes. The enzyme can be used in both free and immobilised states.

The essential physicochemical features of the shift of the chemical equilibrium. On passing from water (as the reaction medium) to a two-phase system with a low content of the aqueous component, a significant shift of the chemical equilibrium was observed[67,68]. One of the causes of the shift of the equilibrium, observed in reactions of the type $A + B \rightleftharpoons C + H_2O$ (where one of the products is water) is self-evident; this is a concentration effect due to the decrease of the concentration of the aqueous reactant in the two-phase system. However, there exists yet another more general source of the shift, namely the change in the effective equilibrium constant as a result of the partition of the reactants between the phases. We shall consider the quantitative characteristics of this phenomenon in relation to certain simple reactions.

The reaction $A \rightleftharpoons B$. In a two-phase system the reactants are partitioned between water and the organic solvent:

$$\begin{array}{ccc} (A & \xrightleftharpoons{K_w} & B)_{aq} \\ \Big\uparrow P_A & & \Big\uparrow P_B \\ (A & \xrightleftharpoons{K_o} & B)_{org} \end{array} \qquad (21)$$

Here the subscripts w and o refer respectively to water and the organic solvent. The effective equilibrium constant of reaction (21), which is equal to the ratio of the overall concentrations of reactants A and B referred to the volume of the entire two-phase system, i.e. $K_{eff} = [B]_{tot}/[A]_{tot}$, can be formulated as follows[100-102]:

$$K_{eff} = K_w \frac{1 + \alpha P_B}{1 + \alpha P_A}, \qquad (22)$$

or

$$K_{eff} = K_o \frac{1 + 1/\alpha P_A}{1 + 1/\alpha P_B}, \qquad (23)$$

where K_W and K_O are the equilibrium constants of reaction (21) in water and in the organic solvent respectively, $\alpha = V_o/V_w$ the ratio of the volumes of the organic and aqueous phases, $P_A = [A]_o/[A]_w$ and $P_B = [B]_o/[B]_w$ are the partition coefficients of the reactants between the phases.

Eqn.(22) shows that K_{eff} changes monotonically with increase of α, namely, depending on the choice of the organic solvent, it can either increase (for $P_A < P_B$) or decrease (for $P_A > P_B$). For fairly high values of α (when the content of the aqueous phase is extremely low), the equilibrium constant tends to a limit $K_W P_B/P_A \equiv K_O$. The partition coefficients of organic compounds between water and commercially available organic solvents are usually between 10^{-4} and 10^4.[103,104] Consequently the limiting shift of the equilibrium (K_{eff}/K_w) can be very considerable in principle.

As an example we shall consider the oxidation of isobutyl alcohol catalysed by alcohol dehydrogenase:

$$\begin{array}{ccc} \{(CH_3)_2CHCH_2OH + NAD \rightleftharpoons (CH_3)_2CHCHO + NADH\}_{water} & & \\ \Big\downarrow P_{alcohol} \qquad\qquad \Big\downarrow P_{aldehyde} & & \\ \{(CH_3)_2CHCH_2OH \qquad\qquad (CH_3)_2CHCHO\}_{org} & & \end{array}$$

This reaction has been thoroughly investigated in water[105]. In a two-phase system[100-102] the position of the equilibrium in this reaction is described by an equation analogous to Eqn.(22), because the cofactor employed does not pass from water to the organic solvent in either the oxidised or in the reduced form (being electrostatically charged).

Consequently the partition coefficients of NAD and NADH are virtually zero. Thus

$$K_{eff} \simeq K_w \frac{1 + \alpha P_{aldehyde}}{1 + \alpha P_{alcohol}}. \qquad (24)$$

The experimental results are presented in Fig.5. Two factors should be noted for the system considered. Firstly, the reaction investigated constitutes a system in which the difference between the hydrophobic properties of the initial and final reactants is very slight. Thus in the water–octanol classical system the partition coefficients of the aldehyde and alcoholic groups differ only by 12%.[103] Nevertheless, it is possible to select a solvent (see Fig.5) such that the partition coefficients of the initial and final reactants differ fairly considerably (for example, due to specific solvation effects). As a result, by varying the nature of the organic phase, it was possible to alter the effective equilibrium constant within very wide limits (by a factor of approximately 100). Secondly, Fig.5 shows that the theoretical curve *1* [plotted on the basis of Eqn.(24) using the partition coefficients of isobutyl alcohol and isobutyraldehyde found in an independent experiment] is in satisfactory agreement with experiment.

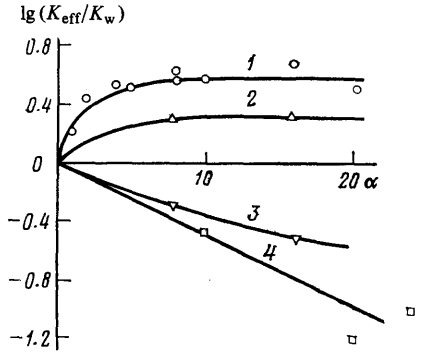


Figure 5. Dependence of the effective constant (K_{eff}) of the reaction involving the oxidation of isobutyl alcohol to isobutyraldehyde catalysed by alcohol dehydrogenase in a two-phase water–organic solvent system on the phase volume ratio α and on the composition of the ethyl acetate–hexane organic phase (ethyl acetate, %): 1) 0; 2) 12.5; 3) 50; 4) 100 (Semenov et al.[100,101]).

The reaction $A + B \quad C + D$. The dependence of the effective equilibrium constants on the ratio of the volumes of the organic and aqueous phases (α), i.e.

$$K_{eff} = K_w \frac{(1 + \alpha P_C)(1 + \alpha P_D)}{(1 + \alpha P_A)(1 + \alpha P_B)}, \qquad (25)$$

is more complex[100-102] than for the previous first-order reaction. Typical instances are presented in Fig.6.

The limiting shift of the equilibrium observed in a two-phase system in the presence of an extremely low water content can be in principle even greater than in the simple reaction A ⇌ B (see above). This is evident because the expression for the limiting shift $K_{eff}/K_w = P_C P_D / P_A P_B$ (at $\alpha \to +\infty$) includes a large number of partition coefficients. However, a more important feature of chemical equilibria involving second order reactions is that the dependence of K_{eff} on α for specific ratios of the partition coefficients can have an extremum (Fig.6). In other words, in a system of two immiscible solvents the effective equilibrium constant may be greater (or correspondingly smaller) than the limiting values characterising the equilibria in each phase. This factor must be taken into account in selecting the optimum conditions for the chemical synthesis (for further details, see below).

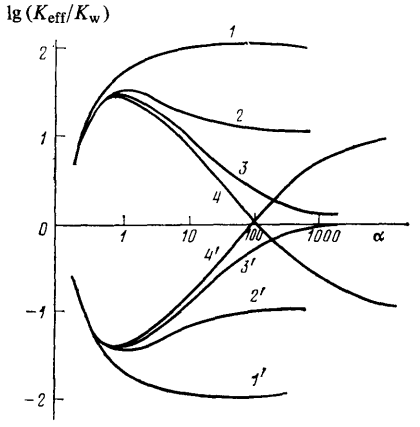


Figure 6. Dependence of K_{eff} for a reaction of the type A + B ⇌ C + D in a water–organic solvent two-phase system on α for certain values of the partition coefficients: 1)–4) $P_A = P_B = 1$, $P_C = 10^2$ [P_D: 1) 1; 2) 10^{-1}; 3) 10^{-2}; 4) 10^{-3}]; 1')–4') $P_C = P_D = 1$, $P_A = 10^2$ [P_B: 1') 1; 2') 10^{-1}; 3') 10^{-2}; 4') 10^{-3}] (Taken from Refs.100–102).

The essential physicochemical nature of this phenomenon (the presence of an extremum) can be discovered very clearly in relation to the following example. We shall assume that the initial reactants are distributed between the phases in such a way that one of them (A) is located fully in one of the phases (water), while the other (B) is located fully in the other (organic solvent). Then the reaction equilibrium in the two-phase system is completely displaced to the left ($K_{eff} = 0$) whatever the equilibrium constant in each phase separately. The reason for this is evidently that the reactants A and B, being separated in space, cannot interact. On the other hand, the equilibrium is fully displaced to the right ($K_{eff} \to \infty$ regardless of the final equilibrium constants in a particular phase) if the final products prove to be completely separated from one another, i.e. when one of the products (for example C) is concentrated entirely in water, while the other (D) passes to the organic solvent.

The extremum of the equilibrium in the two-phase system has been observed experimentally (by varying the ratio of the volumes of the aqueous and organic phases) in relation to the α-chymotrypsin-catalysed synthesis of the ethyl ester of *N*-benzoyl-L-phenylalanine (from ethanol and the corresponding acid)[100-102]. In water the yield of the ester is negligible[106,107]. At the same time in a two-phase system (for the optimum ratio of the volumes of water and the organic solvent) the yield was 80, 64, 62, and 26% for chloroform, benzene, carbon tetrachloride, and diethyl ether respectively[100-102]. Thus, as a result of using two-phase systems, it is possible to increase the yield of the ester virtually from zero to a preparative level.

Decrease of the concentration of the aqueous reactant. In reactions such as the synthesis of ethers, esters, amides, peptides, etc. of the type A + B ⇌ C + H_2O one of the products is water. Therefore in aqueous solution their equilibrium is displaced towards the initial reactants as a consequence of the high concentration of water in the system (55.5 M). On passing to two-phase systems, the water content diminishes; as a result of this, the yield of the product C should in principle increase.

However, one should bear in mind that in a two-phase system the yield of the product C depends on the concentration of water in two ways: not only via the Law of Mass Action, i.e. $[C]_{tot} = K_{eff}[A]_{tot}[B]_{tot}/[H_2O]_{tot}$, but also via the equilibrium constant determined by a function of the type of (25) and hence depending on α. Ultimately we have[100-102]

$$[C] = K_{eff}\frac{[A][B]}{[H_2O]} = K_w\frac{[A][B](1+\alpha P_C)(1+\alpha)}{55.5(1+\alpha P_A)(1+\alpha P_B)}. \quad (26)$$

According to this equation, the dependence of [C] on α can be very complex (Fig.7). In particular, for certain ratios of the partition coefficients there is actually a decrease of the yield of the product C with decrease of the concentration of the second product (water) in the system. This is because the effective equilibrium constant diminishes to a greater extent with increasing α than the overall concentration of water in the system [see Eqn.(26)].

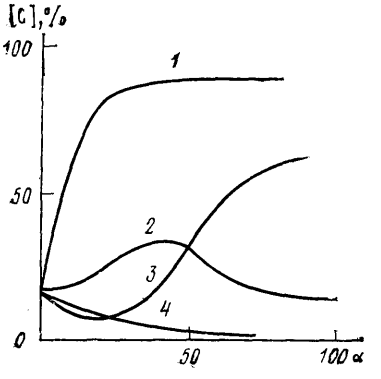


Figure 7. Dependence of the yield of the product C in a reaction of the type A + B ⇌ C + H_2O in a two-phase water–organic solvent system on α for the following partition coefficients: 1) $P_A = P_B = 1$, $P_C = 50$; 2) $P_A = P_B = 0.1$, $P_C = 0.01$; 3) $P_A = 10$, $P_B = 0.01$, $P_C = 1$. 4) $P_A = P_B = 1$, $P_C = 0.1$; it was assumed that $K_W = 10$ (from Martinek et al.[102]) in all cases.

The shift of ionic equilibria. The occurrence of many reactions involves the ionisation of the reactants, for example,

$$\left.\begin{aligned} HA + B &\underset{K'_{eq}}{\overset{K_{eq}}{\rightleftharpoons}} C + D, \text{ where } HA \overset{K_a}{\rightleftharpoons} H^+ + A^- \\ A + B &\underset{K'_{eq}}{\overset{K_{eq}}{\rightleftharpoons}} C + D, \text{where } B + H^+ \overset{K_b}{\rightleftharpoons} BH^+. \end{aligned}\right\} \quad (27)$$

On passing from water to two-phase systems, a change is to be expected not only in the equilibrium constant of the chemical reaction proper (K_{eq}) but also in the equilibrium constants of the ionisation processes (K_a or K_b). As a result, the shift of the equilibrium of the overall process will be evidently determined by the changes in all the constants and will therefore depend on the pH.

In this Section we shall analyse the physicochemical causes of the changes in the constants of ionic equilibria in two-phase water–organic solvent systems relative to aqueous solutions and we shall also consider the possibilities arising in this instance for increasing the yield of products in enzyme-catalysed thermodynamically unfavourable synthetic reactions.

We shall consider, for example, the ionisation of an acid in a two-phase water–organic solvent system[108,109]:

$$\begin{array}{l}(HA \underset{}{\overset{K_a}{\rightleftharpoons}} H^+ + A^-)_{aq} \\ \downarrow\uparrow P_{HA} \\ (HA)_{org}\end{array} \quad . \tag{28}$$

Here we shall assume that virtually only the uncharged form of the acid or base dissolves in the organic phase. This hypothesis is as a rule valid (see for example, Leo et al.[103]). The only exceptions are the highly polar solvents which are capable of extracting from water charged compounds in the form of ion pairs[110].

The ionisation constant of an acid in a two-phase system will be defined in the usual way by the Henderson–Hasselbach equation:

$$(pK_a)_{eff} = pH - \lg \frac{[A^-]_{tot}}{[HA]_{tot}},$$

where $[A^-]_{tot}$ and $[HA]_{tot}$ are the overall concentrations of the ionised and unionised forms of the acid respectively, calculated relative to the volume of the entire two-phase systems, and the pH characterises the aqueous phase. We then have[108,109]

$$(pK_a)_{eff} = pK_a + \lg(1 + \alpha P_{HA}). \tag{29}$$

Similarly for the protonation of a base B in a two-phase system we have

$$\begin{array}{l}(B + H^+ \underset{}{\overset{K_b}{\rightleftharpoons}} BH^+)_{aq} \\ \downarrow\uparrow P_B \\ (B)_{org}\end{array} \tag{30}$$

and we obtain[108,109] the following expression for the effective equilibrium constant:

$$(pK_b)_{eff} = pK_b - \lg(1 + \alpha P_B). \tag{31}$$

Thus in two-phase water–organic solvent systems, the pK_a for the acid increases by an amount $\lg(1 + \alpha P_{HA})$ and the pK_b for the base decreases correspondingly by an amount $\lg(1 + \alpha P_B)$. The partition coefficients of organic acids and bases can reach[103,104] (10^2–10^4). Consequently, in a system containing, for example, 1 vol% of water ($\alpha = 100$) the shift of the effective pK can amount to 4–6 pH units.

The ionisation equilibria of the model compounds 2,4-dinitrophenyltryptophan (acid) and Neutral Red(base) have been investigated[108] in two-phase water–organic solvent systems. It has been shown that, firstly, the effective pK in such systems is indeed displaced relative to aqueous solutions and the experimental shift reaches five or more pH units. Secondly, the experimental dependence of $pK_{b,two\text{-}phase}$ of Neutral Red on α is described satisfactorily by the theoretical curve based on Eqn.(31) using the partition coefficient P_B found in an independent experiment.

We shall now consider how the shift of the pK of the reactants can influence the equilibria of the chemical reactions occurring in two-phase water–organic solvent systems and what possibilities arise in this instance for increasing the yield of the desired product.

The attainment of the coincidence of the pH optima of the efficiency of the catalyst and of the equilibrium of the catalysed reaction. The situation frequently arises where the pH optimum of the stability and catalytic activity of the enzyme is significantly removed from the pH values which favour thermodynamically the synthesis of the given product. As an example, one may point to the synthesis of β-lactam antibiotics (the thermodynamic pH optimum is in the range 3–5),[88] 4-p-nitroanilides (with a pH optimum of 2–3), and esters of *N*-substituted aminoacids whose synthesis is favoured by pH values below 3.[106,107,111] At the same time the majority of enzymes capable of catalysing these synthetic reactions (penicillin amidase, trypsin, α-chymotrypsin, and other proteases) are active and stable only at neutral (or nearly neutral) pH. This contradiction can be resolved by employing two-phase water–organic solvent systems rather than water as the reaction medium.

As an example, we shall consider the synthesis of the ethyl ester of *N*-benzoyl-L-phenylalanine catalysed by α-chymotrypsin:

$$\begin{array}{l}R{-}COOH + EtOH \rightleftharpoons R{-}COOEt + H_2O \\ \downarrow\uparrow K_a \\ R{-}COO^-\end{array} \tag{32}$$

Fig.8 illustrates the pH dependence of the equilibrium constant of this reaction in water (curve *1*).[106] Evidently the synthesis is favoured only by pH values below 3, while at neutral and nearly neutral pH (i.e. under the conditions where α-chymotrypsin functions) the equilibrium is almost wholly displaced towards the initial substances; the fact that one of the reactants (the acid) is dissociated under the given conditions plays a significant role in this instance. Thus in water the enzymatic reaction is of no preparative value.

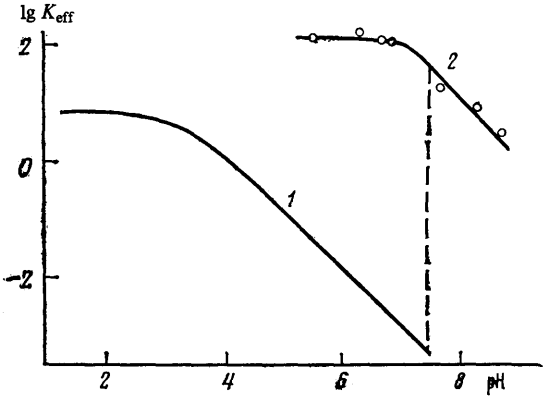


Figure 8. pH dependence of the equilibrium constant of the reaction involving the synthesis of the ethyl ester of *N*-benzoyl-L-phenylalanine in water (curve *1*) and in the chloroform—5 vol.% of water two-phase system (curve *2*)[108,112].

On passing to two-phase water–organic solvent systems[108,112,113], the effective pK_a for the acid increases [see Eqn.(29)], so that the pH dependence of the equilibrium constant shifts towards neutral or alkaline pH. Fig.8 illustrates the pH dependence of the equilibrium constant of reaction (32) in the chloroform +5 vol.% of water two-phase system (curve *2*).

Evidently, compared with aqueous solutions, the pK for the acid has increased by more than three units (see the shift of curve *2* to the right along the abscissa axis compared with curve *1*). As a result, it was possible to achieve the coincidence of the pH thermodynamically favourable for the synthesis and the pH optimum of the catalytic activity and stability of α-chymotrypsin (see the dashed line, pH 7.5). In addition, the limiting, i.e. pH-independent, equilibrium constant has also increased (by more than an order of magnitude) (see the upwards shift of curve *2* along the ordinate axis). The reason for this is that the product (the ester) is preferentially extracted from water into the organic phase. Ultimately the overall change in the equilibrium constant at pH 7.5 (dashed line in Fig.8) is by approximately five orders of magnitude. This is why it has become possible to drive the hydrolytic reaction almost wholly towards synthesis at neutral pH. Thus the yield of the ester in the given system is 80–100% (depending on the reactant concentrations) while in water it does not exceed 0.01%.

Peptide synthesis. An example of reactions involving di-iogenic compounds may be the synthesis of the peptide linkage:

$$\begin{array}{ccc} R_1COOH + R_2NH_2 & \rightleftharpoons & R_1CONHR_2 + H_2O \\ \downarrow\uparrow K_a \quad\quad \downarrow\uparrow K_b & & \\ R_1COO^- \quad R_2NH_2^+ & & \end{array} \qquad (33)$$

The pK_a for carboxylic acids are usually in the range 3–4 and the pK_b for amines are 8–10.[50,107,114] Consequently, in water, over the entire pH range, at least one of the initial reactants exists almost entirely in a charged form. As a result, the equilibrium of the overall reaction is almost wholly displaced to the left, towards hydrolysis[107].

On passing to two-phase water–organic solvent systems, the effective pK_a for the acid as a rule increases and the pK_b for the base diminishes (see above), which implies that at neutral pH the fraction of the uncharged forms of both the acid and the amine increases to some extent[108,109]. Consequently the equilibrium of reaction (33) should be displaced to the right, towards synthesis. The second source of the shift of the equilibrium is that the peptide is as a rule extracted from water to the organic solvent more effectively than the initial reactants. Thirdly and finally, the equilibrium yield of the product in reaction (33) in a two-phase water–organic solvent system should also increase owing to the decrease of the water content.

We tested this approach[108,109,115,116] in relation to the α-chymotrypsin-catalysed synthesis of *N*-acetyl-L-tryptophanyl-L-leucine amide:

$$\text{N—Ac—}L\text{-Trp} + L\text{-LeuNH}_2 \rightleftharpoons \text{L—Ac—}L\text{-Trp—}L\text{-LeuNH}_2 + H_2O.$$

On passing from water to the two-phase system ethyl acetate + 2 vol.% of water, the equilibrium constant of the synthetic reaction increased by more than three orders of magnitude (cf. curves *1* and *3* in Fig.9). As a result, the reaction equilibrium was displaced considerably to the right, which made it possible to synthesise the dipeptide almost quantitatively in water the yield does not exceed 0.1% other conditions being equal.

Synthesis of ionic products. It would appear that the two-phase approach to preparative organic synthesis is inapplicable to reactions where the products are ions because they would not pass from water to the organic phase and hence would not be distributed throughout the system. However, this difficulty can be overcome by selecting for the ionic reactants hydrophobic counterions, as is done, for example, in the chemistry of nucleotides[117] and has also proved useful in the radioactive analytical method[118]. We tested this approach in relation to the synthesis of glycerophosphate from inorganic phosphate and glycerol[67]. The reaction was catalysed by alkaline phosphatase using tetrabutylammonium as the hydrophobic counterion for the phosphates. In the chloroform–water two-phase system the yield of glycerophosphate was more than 30%,[67] while in water (in the absence of the organic phase but otherwise under the same conditions) the yield was negligible[83].

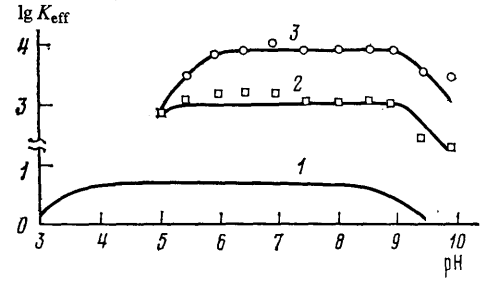


Figure 9. pH dependence of the equilibrium constant of the reaction involving the synthesis of *N*-acetyl-L-tryptophanyl-L-leucine amide in water (curve *1*) and in the ethyl acetate–water two-phase system containing 17 vol.% (curve *2*) and 2 vol.% (curve *3*) of water[108,115].

The enzymatic two-phase method is also applicable to other processes of practical importance involving ionic products, such as the modification of antibiotics[119], the synthesis of a dipeptide from free aminoacids[120], and the separation of a racemic mixture of free aminoacids[121].

General remarks concerning the choice of experimental conditions. Theoretical study[100–102] of the equilibria of chemical reactions in two-phase water–organic solvent systems permits the following conclusion: the equilibrium of a chemical reaction in a two-phase system is in general determined by the equilibrium constant of this reaction in one of the phases, the partition coefficients of the initial and final reactants, and the ratio of the volumes of the organic and aqueous phases. Consequently, knowing the equation describing the equilibria of the reactions in the two-phase systems and the partition coefficients (from the literature or from independent experiments), it is possible to calculate K_{eff} and hence the yield of the reaction products [see, for example, Eqns.(22), (25), and (26)]. Unfortunately the amount of information in the literature about the partition coefficients of various substances is at present inadequate and the available information is not always reliable[103,104]. In addition one must bear in mind that at high concentrations of reactants the latter can themselves alter the reaction medium and the distribution of the reactants (and hence the effective reaction equilibrium) will exhibit deviations from a simple (ideal) model[122].

It is important to be able to predict the mode and extent of the change in the equilibrium in a two-phase system relative to water because the dependence of K_{eff} (and of the yield of the chemical reaction products) in a two-phase system on the volume ratio of the phases (α) can be fairly complex. Consequently it can hinder the selection of the experimental conditions for the synthesis. In this connection, we draw attention to two factors.

1. For certain ratios of the partition coefficients, K_{eff} for reaction (4), observed in a two-phase system, can be significantly greater (Fig.6, curves 2–4) or correspondingly smaller (Fig.6, curves 2′–4′) than the equilibrium constants of the same reaction in each phase. We shall analyse this phenomenon in greater detail (quantitatively) in relation to a two-phase system where $K_W = K_O$, i.e. we shall assume that the equilibrium constant is the same in both immiscible solvents. The partition coefficients will be varied in the range of reasonable values from 10^{-5} to 10^5 (cf. Leo et al.[103]).

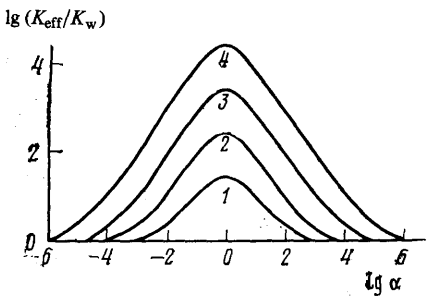


Figure 10. The extremum in the relation between K_{eff} for a reaction of the type A + B ⇌ C + D in the water–organic solvent two-phase system on the phase volume ratio (α) for the following partition coefficients: 1) $P_A = P_B = 1$, $P_C = 10^2$, $P_D = 10^{-2}$; 2) $P_C = 10^3$, $P_D = 10^{-3}$; 3) $P_C = 10^4$, $P_D = 10^{-4}$; 4) $P_C = 10^5$, $P_B = 10^{-5}$ (from Martinek et al.[102]).

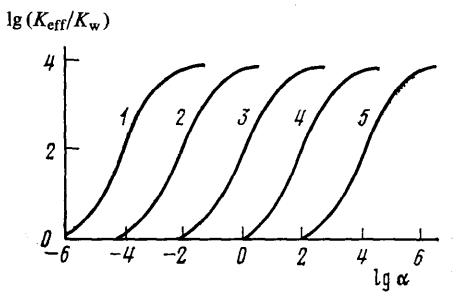


Figure 11. Examples of the S-shaped relation between K_{eff} for a reaction of the type A + B ⇌ C + D in a two-phase water–organic solvent system on α for the following partition coefficients: 1) $P_A = P_B = 10^3$, $P_C = P_D = 10^5$; 2) $P_A = P_B = 10$, $P_C = P_D = 10^3$; 3) $P_A = P_B = 0.1$, $P_C = P_D = 10$; 4) $P_A = P_B = 10^{-3}$, $P_C = P_D = 0.1$; 5) $P_A = P_B = 10^{-5}$, $P_C = P_D = 10^{-3}$ (from Martinek et al.[102]).

Fig.10 shows how the effective value of K_{eff} varies in a particular instance with the phase volume ratio α. Evidently the maximum effective equilibrium constant, observed for a reaction of the type A + B ⇌ C + D in a two-phase system, can exceed by a factor greater than 10^4 the corresponding equilibrium constants for the same reaction in each of the phases. Consequently the application of two-phase systems as reaction media can be particularly useful for increasing the yield of the desired product in reactions (not necessarily enzymatic) where the equilibrium is not displaced in the required direction in any of the solvents which are available and suitable for the given reaction.

2. In selecting the conditions for the synthesis, one should also bear in mind that the dependence of K_{eff} on α may be S-shaped (even in terms of non-logarithmic coordinates)[102], i.e. over a certain range of values of α the reaction equilibrium is as it were insensitive to a change in the medium. This can be seen from Fig.11, where we analysed the case where $10^4 K_W = K_O$. Evidently, depending on the partition coefficients (which were varied in the range of reasonable values from 10^{-5} to 10^5),[103] the shift of the chemical equilibrium is observed both for a negligible content of the organic phase ($\alpha = V_O/V_W \cong 10^{-5}$, curve 1) and for comparable amounts of the phases ($\alpha \cong 1$, curves 3), or even, finally, in the absence of water from the system ($\alpha \cong 10^5$, curve 5). In each case it is convenient to employ different methodological procedures to establish the two-phase system. Thus two-phase systems can be formed in the following way.

(a) For systems with a low content of the organic phase ($\alpha \ll 1$), this can be, for example, an aqueous solution of a surfactant forming micelles†; the internal (hydrophobic) region of the micelles can serve as the organic phase[123].

(b) For systems with a low water content ($\alpha \gg 1$), the enzymes should apparently be enclosed in "inverted" micelles of surfactants in an organic solvent[16,98,125].

(c) Systems containing comparable amounts of the organic and aqueous phases can be set up, as already mentioned above (see Section I), in the form of an emulsion of an aqueous solution of the enzyme in an organic solvent or as a suspension in the same solvent of porous particles impregnated with an aqueous solution of the enzyme. When an emulsion is used, the question of the specific interface is extremely important: the greater the specific interface, the faster the diffusion of the reactants through the interface, which has a favourable influence on the reaction kinetics; on the other hand, under these conditions the inactivation of the catalyst (enzyme) can be accelerated as a result of its adsorption at the interface[126]. In this instance one can employ a simple two-layer system.

Generally speaking, any substance capable of forming a two-phase (or pseudo-two-phase system) can be used as the "organic" phase. For example, a water-insoluble polymer can be used for this purpose[127,128].

V. THE PRESENT STATE OF ENZYME CATALYSIS AND THE PROSPECTS FOR ITS INTRODUCTION INTO ORGANIC SYNTHESIS

It is seen from the above survey that enzymes have been used very successfully without additional stabilisation (in relation to denaturation by the reaction medium) in a whole series of synthetic reactions. This has also been promoted by the development of physicochemical approaches whereby the yield of the product can be increased directly under conditions favourable (optimal) for biocatalysis.

It follows from the data in the present review that for the purposes of organic synthesis about 50 enzymes have already proved useful, mainly in the following processes (references are given only to reviews and the latest surveys).

†In the case of micellar systems it is possible to speak of the presence of two phases only as a matter of convention because there is no visible interface. It is therefore more appropriate to speak of "pseudo-two-phase" systems[123]. Nevertheless all the characteristics of the shift discussed above obtain in this instance (see, for example, Martinek and coworkers[124,125]).

1. The Synthesis of Oligo- and Poly-nucleotides

The methods for the chemical synthesis of the internucleotide linkage have been as yet inadequately developed and it is virtually impossible to synthesise a polynucleotide containing several tens of units by a purely chemical procedure[129]. Much attention is therefore devoted in the literature to enzymatic methods for the synthesis of oligo- and polynucleotides. In the synthesis of oligoribonucleotides and oligodeoxyribonucleotides use is therefore made of ribonuclease[24,129–132]:

$$N{>}p + N' \xrightarrow{\text{RNAase}} NpN', \qquad (34)$$

polynucleotide phosphorylase[24,129,130,133]:

$$I + NDP \xrightarrow{\text{PNPase}} IpN + P_i \qquad (35)$$

or RNA ligase[129,134]:

$$NpN' + pN''pN'''p \xrightarrow{\text{RNA ligase + ATP}} NpN'pN''pN'''p\ . \qquad (36)$$

Here N >p is the nucleotide 2′,3′-cyclic phosphate, N the nucleoside, NDP the nucleoside diphosphate, NpN′ the dinucleoside monophosphate, and I the initiator (primer) molecule (usually a dinucleotide).

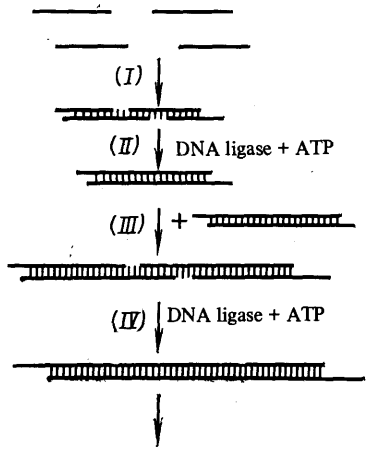


Figure 12. Illustration of the "method of sticky ends". Horizontal lines—sequence of nucleotides joined by covalent bonds; vertical lines—complementary non-covalent (hydrogen) bonds.

For reaction (34), preference is given to non-specific ribonucleases as the catalyst. This makes it possible to synthesise oligonucleotides containing a wide variety of nucleosides, including some which are not encountered in nature. Reaction (35) may involve the extremely undesirable polymerisation process and several approaches have been developed for its suppression[24]. Reaction (36) has been discovered comparatively recently and so far has been hardly used.

Khorana and coworkers[135,136] developed a method for the synthesis of double-stranded polynucleotides with a definite sequence, which has come to be called the "method of sticky ends". His idea can be understood from Fig.12. According to this method, in the first stage the initial oligonucleotides (with a length equivalent to 5–15 units) form a double-stranded complex as a result of complementary non-covalent interactions [stage (1)]. Next, the 3′- and 5′-ends in the resulting complex, which have approached one another in space, are joined by covalent linkages under the influence of DNA ligase [stage(II)]. All the fragments from which the final polynucleotide is to be made up are synthesised in this way and are linked initially via complementary non-covalent interactions [stage (III)] and then also by covalent bonds [stage (IV)]. Using this scheme, Khorana and coworkers synthesised the structural gene of alanine tRNA [135] and the complete gene of suppressor tyrosine tRNA.[136]

2. Regeneration of ATP

Adenosine 5′-triphosphate (ATP) is the substrate of many enzymatic reactions and is widely used in research and in recent years also in enzymatic organic synthesis. In connection with the latter factor, the problem of the regeneration of ATP from ADP and (or) AMP arose.

Among the fairly large number of systems proposed for this purpose, two reactions, catalysed either by acetylphosphokinase[137–139], i.e.

$$ADP + \text{acetylphosphate} \xrightarrow{\text{acetylphosphokinase}} ATP + \text{acetate},$$

or by carbamoyl phosphate kinase[140],

$$ADP + \text{carbamoyl phosphate} \xrightarrow{\text{carbamoyl phosphote kinase}} ATP + \text{carbamate},$$

must be recognised at present as the most suitable.

If AMP is used as the initial reactant, then adenylate kinase must also be introduced into the system[137]:

$$AMP + ATP \xrightarrow{\text{adenylate kinase}} 2ADP.$$

Laboratory devices for the regeneration of ATP have been constructed on the basis of acetylphosphokinase and adenylate kinase immobilised on Sepharose and carbamoyl phosphokinase immobilised on glass[138,140].

3. Synthesis of Labelled Compounds

Compounds containing heavy or radioactive atoms in specific positions within their molecules have found extensive applications in chemistry and biology for the investigation of the mechanisms of chemical and enzymatic reactions, metabolic pathways, molecular structures, etc. Enzymes have been used on an increasing scale in recent years for the synthesis of compounds of this kind. The application of enzymes has the following principal advantages.

Firstly, *specificity*. In the synthesis of labelled compounds it is extremely important to introduce the label into rigorously defined positions within the molecule. The unique specificity of enzymes as a rule permits this. Apart from the high purity of the desired product, the expensive radioactive material is not consumed on side reactions in enzymatic synthesis.

Secondly, *high rate*. At the present time it appears extremely promising to use as labels the so-called short-lived isotopes, for example ^{11}C (half-life $T_{1/2} = 20.3$ min), ^{13}N ($T_{1/2} = 10$ min), ^{15}O ($T_{1/2} = 2$ min), and others. However, as a consequence of the high rate of decomposition of such isotopes, purely chemical synthetic methods were frequently ineffective. The synthesis of compounds containing short-lived isotopes became possible as a result of the employment of enzymes[141].

Thirdly, *mild conditions*. Enzymatic reactions proceed under mild, as a rule, physiological conditions. This is significant, for example, in the synthesis of labelled amino-acids (there is no racemisation) or proteins (there is no denaturation).

Tens of examples of the successful employment of enzymes for the synthesis of various labelled compounds have now been described.

Proteins. The following system is normally used in the synthesis of labelled protein derivatives[142-144]:

$$\text{protein} + K^{125}I + H_2O_2 \xrightarrow{\text{peroxidase}} \text{protein} - {}^{125}I.$$

The enzyme is used in the soluble or (better) immobilised[144] form.

Aminoacids. The initial reactants for the synthesis of labelled aminoacids are α-ketoacids and $\overset{*}{N}H_3$:[141,145-149]

$$R{-}\underset{\underset{O}{\|}}{C}{-}COOH + \overset{*}{N}H_3 + NADH \rightleftarrows L\text{-}R{-}\underset{\underset{{}^*NH_2}{|}}{CH}{-}COOH + NAD^+.$$

The reaction is catalysed by glutamate dehydrogenase obtained from ox heart, which (in contrast to the enzyme from other sources) exhibits a broad substrate specificity.

Nucleoside triphosphates. The problem of the synthesis of nucleoside triphosphates containing ^{32}P in the α-, β-, or γ-positions only has been solved with the aid of enzymes[150-153].

Sugars. Enzymes have been used to synthesise certain commercially unavailable sugars from commercial preparations of labelled glucose[47,154].

4. Synthesis of Oligopeptides

In the 1930's Bergmann showed for the first time that proteolytic enzymes can affect not only the hydrolysis but also the synthesis of peptides. In recent years the number of publications on this topic has increased sharply, since enzymatic or combined (enzymatic plus chemical) methods came to be regarded as a serious alternative to purely chemical synthesis of the peptide linkage. The advantages of the enzymatic method include the following: (a) the absence of racemisation; (b) mild reaction conditions which rule out degradation of labile compounds; (c) the absence of the need to protect the functional groups in the aminoacid side chains: (d) the absence of the need to activate the reacting groups.

Apart from the large number of model oligopeptides[29,30,34-42,57,58,64,65,89-92], important biologically active compounds such as angiotensin[39], encephalins[42,155], and human insulin[64,65] have been synthesised with the aid of enzymes.

The range of enzymes employed has been greatly extended: whereas up to 1970 only papain and chymotrypsin were used as catalysts, nowadays trypsin, pepsin, subtilisin, ficin, bromelain, carboxypeptidase (for the removal of protecting groups[156]), thermolysin, and bacterial metalloproteinases have also found applications.

5. The Synthesis and Modification of β-Lactam Antibiotics

The enzymatic method for the modification of β-lactam antibiotics in order to improve their properties, developed on a wide scale in recent years, appears to be extremely promising. According to this procedure[5,15], in the first stage the natural β-lactam antibiotics are subjected to penicillin amidase-catalysed hydrolysis in order to obtain the so-called nucleus of the antibiotic: 6-aminopenicillanic acid (in the case of penicillins) or 7-aminocephalosporanic acid) (in the case of cephalosporins). In the second stage the nucleus of the antibiotic is acylated (using penicillin amidase as the catalyst):

$$R^1{-}\underset{\underset{O}{\|}}{C}{-}N{-}\underline{\overline{\text{nucleus}}} \underset{-R^1COOH}{\overset{+H_2O}{\rightleftarrows}} H_2N{-}\underline{\overline{\text{nucleus}}} \xrightarrow{+R^2COOH} R^2{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{H}{|}}{N}{-}\underline{\overline{\text{nucleus}}} \quad (37)$$

In the second, acylation stage the yield of the product can be increased by carrying out the reaction in a weakly acid medium (a pH of 4.5–5.0 is optimum for the synthesis in most instances) or using as the acylating agent not the free acid but its activated derivatives.

By varying the acyl group R^2, it is possible to improve specifically the properties of antibiotics—to extend the spectrum of their activity, to increase their stability in the organism, and to reduce their allergenic effect. Several tens of "semisynthetic" antibiotics have been obtained in this way[5,15,87,88,157].

6. Modification of Steriods

Enzymes, cells, or unpurified extracts are also used for the modification of steroids[158-164].

7. Industrial Processes

Together with the laboratory developments discussed above, a series of technological (industrial) processes involving immobilised enzymes have been set up recently: (a) the synthesis of L-aspartic acid using immobilised microbial cells containing aspartase[14]; (b) the synthesis of L-malic acid using immobilised microbial cells containing fumarase[15]; (c) the synthesis of 6-aminopenicillanic acid using immobilised penicillin amidase[15]; (d) the separation with the aid of immobilised aminoacylase of racemic mixtures of aminoacids (obtained by a chemical, non-enzymatic procedure)[15,19]; (e) the synthesis of D-aminoacid derivatives with the aid of immobilised hydantoinase[15].

There are also large-scale industrial processes which go beyond the classical framework of organic synthesis and are more in the nature of the industrial manufacture of food products; (f) the preparation of glucose–fructose syrups using immobilised glucose isomerase[165,166]; (g) decomposition of lactose (the preparation of lactose-free milk) with the aid of lactase[15].

Certain processes have been developed only on pilot apparatus: (h) the synthesis of glucose from partial starch hydrolysates using immobilised glucoamylase[167]; (i) the synthesis of glucose and (or) ethanol from cellulose using cellulase[168]; (j) the preparation of glucose–fructose syrups from sucrose with the aid of immobilised invertase[15].

The Table, which we took from Sweigart and Dale[14] and supplemented by Klesov's data[169], gives a list of organisations which have set up these industrial (or pilot) processes.

It may seem surprising that a review of organic syntheses includes also the "food" processes (f)–(j). The need for this combined approach to the analysis of the present state of the problem (the introduction of enzymes into industrial processes) arises partly from the fact that enzyme catalysts have long been used in the food industry and at the present time (1976–1979) the food industry is the main consumer of the manufactured enzymes[13]. However, the principal factors which led us to consider, as far as possible, the most complete picture of the technological processes catalysed by enzymes are as follows. Firstly, the use of enzymes is beginning to break up the usual framework of organic synthesis. Secondly, any enzymatic food process (processes) gives rise to

new prospects for the large-scale preparation of raw material for chemical engineering, namely ethanol (and possibly also glucose). Finally, on the basis of processes already introduced, it is easier to predict certain economic factors. Evidently modern microbiological industry is already (1976) able to ensure the manufacture of enzymes in amounts running into hundreds of tons annually (at a cost of approximately 150 million dollars)[13]. However, the contribution of the ensyme to the overall cost of the product is in many instances insignificant[13,14].

The use of immobilised enzymes in large-scale (industrial) (L) and pilot plant (P).

Firm	Process*									
	a	b	c	d	e	f	g	h	i	j
ANHEUSER BUSCH (BRD)	—	—	—	—	—	L	—	—	—	—
CLINTON CORN (USA)	—	—	—	—	—	L	—	—	—	—
CAR MI (USA)	—	—	—	—	—	L	—	—	—	—
CORNING GLASS (USA)	—	—	—	P	—	L	L	P	—	P
US ARMY NATICK CENTER (USA)	—	—	—	—	—	—	—	—	P	—
DENKI KAGAKU (Japan)	—	—	—	—	—	P	—	—	—	—
DIAMOND SHAMROCK (USA)	—	—	—	—	—	—	P	—	—	—
GIST-BROCADES (Netherlands)	—	—	—	—	—	L	P	P	—	P
GULF OIL (USA)	—	—	—	—	—	—	—	—	P	—
HAMEEN PERUNA (Finland)	—	—	—	—	—	L	—	—	—	—
ICI (England, USA)	—	—	—	—	—	L	—	—	—	—
LEHIGH UNIVERSITY (USA)	—	—	—	—	—	—	P	—	—	—
NOVO (Denmark)	—	—	—	—	—	L	—	—	—	—
SANMARSU (Japan)	—	—	—	—	—	L	—	—	—	—
SNAM PROGETTI (Italy)	—	P	L	P	L	P	L	P	P	—
TANABE SEIYAKU (Japan)	L	L	L	L	—	—	—	—	—	—
VALIO (Finland)	—	—	—	—	—	—	P	—	—	—

*For the classification of the processes, see text.

For the introduction of biocatalysis into industrial processes (in which economic factors play a decisive role) on a wider scale, it is naturally necessary to improve further processes involving the microbiological synthesis and isolation of enzymes, methods for the preparation of carriers and the immobilisation of enzymes on them, enzymatic reactors, etc. However, the key problems at the present stage are the stabilisation of enzymes (see, for example, Martinek and Berezin[170]) and then the regeneration of cofactors, the use of polyenzyme systems, and the immobilisation of micro-organisms.

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Polyfluorinated Arenonium Ions

V.D.Shteingarts

This novel type of arenonium ions plays a key role in the isomerisation and electrophilic reactions of aromatic compounds. Methods for their generation, the investigation of their electronic structure by means of fluorine-19 nuclear magnetic resonance, and the influence of structural factors on their relative stability are discussed. Results on the chemical reactions of polyfluorinated arenonium ions, opening up paths for their synthetic use, are summarised. A list of 74 references is included.

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I. INTRODUCTION

A most important stage in studying the mechanism of the reactions of aromatic compounds with electrophilic agents, which has been responsible for a recently established and extremely fertile direction of research in this field, has been the development of methods for generating long-lived arenonium ions that in some degree model intermediate species in these reactions. The progress made[1] has provided an experimental basis for earlier views on the intermediate formation of σ-complexes during electrophilic reactions of aromatic compounds and has revealed the role of isomerisation of these species as one factor governing the dependence of the final result on the reaction conditions; in particular, the isomeric composition of the reaction products depends on the contribution made to the total change by addition of an electrophilic species to a substituted aromatic ring carbon atom (*ipso*-reactions[2]).

ipso-Reactions with electrophilic agents have recently been studied in particular on aromatic polyfluoro-compounds. The immense possibilities for the synthesis of diverse polyfluorinated compounds opened up by the discovery of reactions of this type (those between aromatic polyfluoro-compounds and nitrating reagents have been reviewed[3]) and the trend to their directed use have made necessary a more profound study of the reaction mechanism.

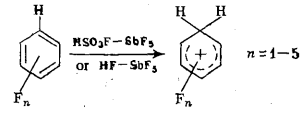
The mechanism of *ipso*-electrophilic reactions of aromatic polyfluoro-compounds suggested initially involves addition of the electrophilic species at a position in the aromatic ring occupied by such an electronegative substitutent as a fluorine atom[3]. The arenonium ion assumed to be formed possesses structural characteristics that are extremely unfavourable for its stability: it contains a large number of fluorine atoms at positions in the unsaturated portion at which the substituent plays no effective part in charge delocalisation by a conjugation mechanism (non-resonance positions†), and also two electronegative substituents together at an sp^3-hybridised site. At the time at which this scheme was proposed stable arenonium ions having such characteristics were unknown. Therefore the generation of ions of this type under "long-lived" conditions, with the aim of demonstrating the very possibility of their existence, would provide one of the most fundamental pieces of experimental evidence in support of the scheme. Results thus obtained are obviously of value not only in studying the chemistry of aromatic polyfluoro-compounds: they are important for understanding the properties of carbocations—species that have a fundamental role in organic chemistry.

† We shall regard as resonance positions those that are involved in delocalisation of the positive charge when the distribution of π-electron density is described in terms of limiting ("resonance") structures.

II. GENERATION OF POLYFLUORINATED ARENONIUM IONS

1. Protonation of Partly Fluorinated Aromatic Compounds

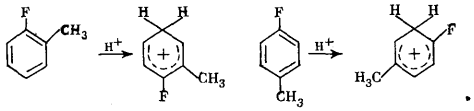
The first polyfluorinated arenonium ions were obtained by this reaction, which was most widely used in the initial state of development of the chemistry of these species (during 1967–1968). The weak basicity of aromatic polyfluoro-compounds required the use of a "superacid"—a solution of antimony(V) fluoride in fluorosulphuric acid—to achieve a sufficient degree of protonation. Both hydrogen and fluorine-19 nuclear magnetic resonance spectroscopy were used to record the formation of benzenonium ions having two hydrogen atoms as geminal substituents[4–6] when incompletely substituted fluorinated benzenes were dissolved in this acid system:



The orientation of addition of the proton then corresponds to decrease in stability of the arenonium ions as the position of the fluorine atom in the unsaturated part varies in the sequence *para* > *ortho* ≫ *meta*. *o*-Difluorobenzene, 1,2,3,4- and 1,2,4,5-tetrafluorobenzenes, and pentafluorobenzene are hardly protonated at all in this acid system, owing to the strong destabilisation of arenonium ions by a *meta*-fluorine atom. Protonation of these compounds required the use of a stronger acid—a solution of antimony(V) fluoride in hydrofluoric acid—but hexafluorobenzene is not protonated even in this case[7]. Such difficulty of *ipso*-protonation according to the position occupied by a fluorine atom is consistent with subsequent quantum-chemical calculations of the relative stability of fluorobenzenonium ions[8].

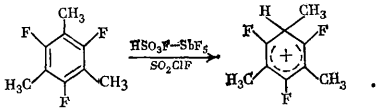
Fluorine-containing methylbenzenes are also protonated at unsubstituted positions[5,6,9]. In cases in which the *ortho*–*para* orienting effects of methyl group and fluorine atom do not coincide the fluorine atom in the resulting arenonium ion

is located in a resonance position, predominantly *para*, while the methyl group occupies the non-resonance *meta*-position[5]:



Because of the high rate of interconversion of isomeric arenonium ions corresponding to protonation of aromatic compounds the above rules apply to equilibrium proportions of isomers. However, isomeric ions differ in the nature of the substitutents at two or more positions, so that the relative effects of substituents at any one of them on the stability of the ion cannot be assessed. Therefore the orientation involved in the protonation of *o*- and *p*-fluorotoluenes cannot be interpreted as indicating that a fluorine atom has a stronger stabilising influence than a methyl group in the resonance arrangement. Determination of the relative stabilising effects of these substituents by comparing the relative stabilities of arenonium ions differing in the substituent at only one position (Section III) has shown that the methyl group has the stronger stabilising influence.

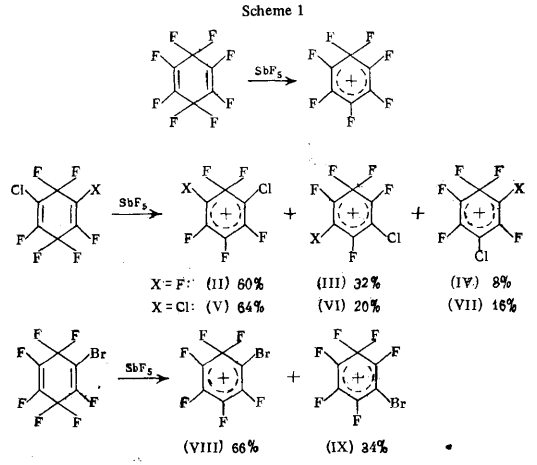
The only example of an aromatic polyfluoro-compound that is completely substituted in the ring and is converted into an arenonium ion on protonation is trifluoromesitylene. In this case, however, a benzenonium ion is formed in which all the fluorine atoms are located in the unsaturated portion[5]:



The above examples show that the arenonium ions containing a fluorine atom attached to an sp^3-hybridised carbon atom cannot be obtained by the protonation of aromatic fluoro-compounds. Such ions have been obtained by using less traditional methods of generating arenonium ions.

2. Action of Antimony(V) Fluoride on Polyfluorinated Dihydro-aromatic Compounds

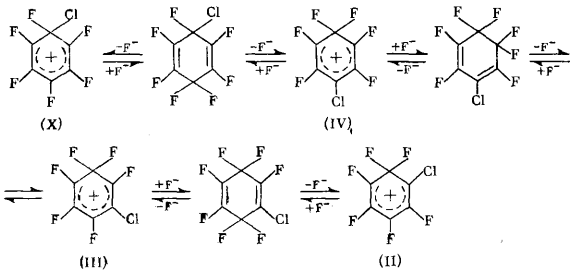
Scheme 1



An approach made earlier to obtain alkyl cations[10,11] has proved useful for generating polyfluorinated arenonium ions having fluorine atoms in an sp^3-hybride node: a fluoride anion is detached by antimony(V) fluoride from the corresponding precursor, in the present case from the polyfluorinated dihydro-aromatic compound. The perfluorobenzenonium ion (I) and its analogues (II)–(IX) containing chlorine or bromine atoms in the unsaturated portion have been generated from polyfluorinated cyclohexadienes in antimony(V) fluoride[12,13] and in sulphuryl chloride fluoride[14–16]. Scheme 1 gives for these analogues the equilibrium proportions established in antimony(V) fluoride solution at 20–40 °C.

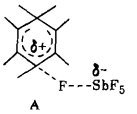
Ions containing a *p*-chloro-substitutent cannont be formed directly from percursors. Their presence in the reaction mixtures indicates the possibility of interconversion of isomeric ions, which apparently occurs by a series of reversible transformations of benzenonium ions into cyclohexadienes[13,14]. The equilibrium character of the proportions given in Scheme 1 is supported by formation of the ion (IV) and of the 1-chlorohexafluorobenzenonium ion (X) in the proportions 9 : 1 when antimony(V) fluoride acts on 3-chloroheptafluorocyclohexa-1,4-diene in sulphuryl chloride fluoride at −90 °C (the latter ion (X) is generated also by the chlorination of hexafluorobenzene—see below). With rise in temperature to −40 °C the ion (X) is converted into (IV), which at −20 °C is in turn converted into the ions (II) and (III), between which the above relation is established. The sequence of interconversions of chlorohexafluorobenzenonium ions when the solution "thaws out" (Scheme 2) indicates the greater ease of addition of a nucleophilic species at the *para*-position in the benzenonium ion [transition from (X) to (IV)] than at an *ortho*-position [conversion of (IV) into (III) and then into (II)], and may well represent the relative electrophilic strengths of the two resonance positions in the cyclohexadienyl fragment[14].

Scheme 2



It follows from the above results that between −90 and −80 °C the addition of a fluoride ion at the *para*-position and hence also the isomerisation of polyfluorinated arenonium ions are slow processes. This means that the proportions in which isomers are formed at these temperatures are kinetically controlled. The action[17] of antimony(V) fluoride on hexafluoro-1-halogenocyclohexa-1,4-dienes in sulphuryl chloride fluoride at −90 °C yields the corresponding hexafluoro-2- and -3-halogenobenzenonium ions in the proportions 1 : 2 and 1 : 3 when the halogen is respectively chlorine and bromine; these differ from the equilibrium proportions of the same ions (Scheme 1) established at −60 °C. In the case of the chloro-compounds complete equilibrium involving the isomer (IV) is established at −20 °C.[17]

If the transition state corresponding to the detachment of a fluoride anion from a cyclohexadiene molecule is assumed to be of the type



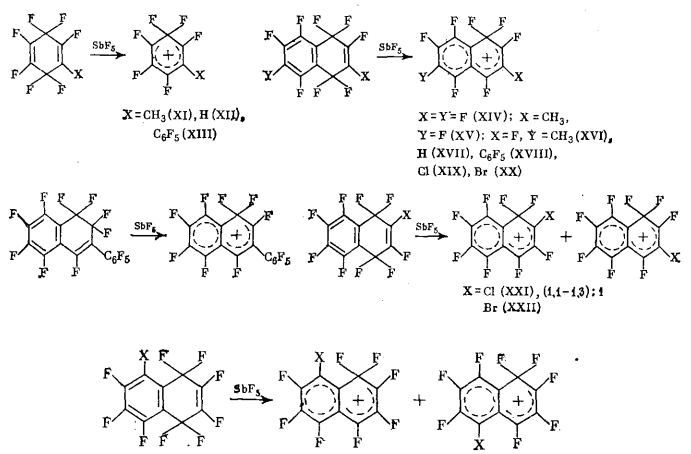
A

the discrepancy between the kinetically controlled and the equilibrium ratios of isomeric ions may indicate that the increase in the positive charge in the cyclohexadienyl system accompanying transformation of the transition state into an

arenonium ion leads to a change in the relative stabilising effects of *o*- and *m*-halogeno-substitutents with respect to the sp^3-hybridised carbon atom[17].

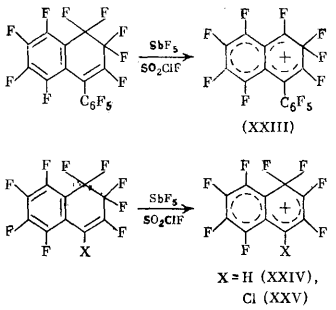
The ions 1,1,2,4,5,6-hexafluro-3-methylbenzenonium (XI),[18] 1,1,2,3,4,6-hexafluorobenzenonium (XII),[16] perfluoro-3-phenylbenzenonium (XIII),[19] and perfluoro-1-naphthalenonium (XIV)[12,13] and many of its substituted analogues[17-19] have been generated by the action of antimony(V) fluoride on the corresponding polyfluorinated cyclohexadienes (Scheme 3).

Scheme 3



The formation of ions (XI), (XV), and (XVI) corresponds to the tendency mentioned in subsection 1 for the methyl group to occupy a non-resonance position if that will make a resonance arrangement of the fluorine atom possible[18]. This also partly explains the preferential non-resonance orientation of the pentafluorophenyl group. In the latter case, however, another possible factor is that resonance involvement of the pentafluorophenyl group in charge delocalisation is apparently diminished by its non-coplanarity with respect to the remainder of the ion, which causes steric interaction of fluorine atoms situated near together[19,20].

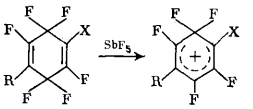
The net effect of these factors is that, with a pentafluorophenyl group substituted on an α-carbon atom in the cyclohexadienyl fragment of a naphthalenonium ion, the napthalen-2-onium ion (XXIII) is formed[21], whereas naphtalen-1-onium ions are usually more stable than naphthalen-2-onium ions[1] (cf. formation of the ions (XXIV) and (XXV) from the corresponding precursors[22]):



The relative stabilising effects of so closely related substituents as the halogen atoms are apparently very sensitively dependent on the structure of the arenonium ion, primarily on the distribution of positive charge in it (cf. the above data on the discrepancy between kinetically controlled and equilibrium proportions of halogenohexafluorobenzenonium ions).

This is evident e.g. in the conclusion from the equilibrium ratios of isomeric 1,1-difluorobenzenonium and 1,1-difluoronaphthalen-1-onium ions that a chlorine or a fluorine atom in a cyclohexadienyl fragment occupies preferentially a resonance position (predominance of the ions (II), (V), (XIII), (XXI), and (XXII) over their isomers), whereas halogen atoms in a β-position in the benzene fragment of naphthalen-1-onium ions are characterised by the opposite tendency (ions (XIX) and (XX)—see above).

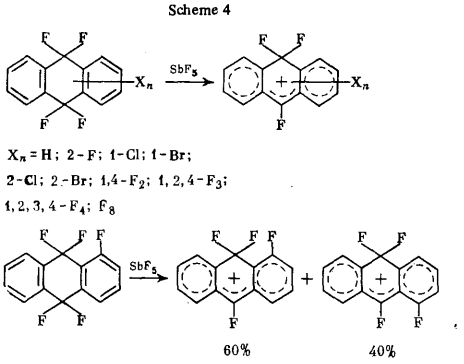
The possibility of generating 5-R-pentafluoro-2-halogenobenzenonium ions (R = CH_3, H) from the corresponding cyclohexadienes was predicted from the above results and then realised[15]:



R = CH_3, X = Cl, Br, CH_3; R = H, X = Cl, Br, H, CH_3 .

The action of antimony(V) fluoride in sulphur dioxide at −20 °C on 9,9,10,10-tetrafluoro-9,10-dihydroanthracenes yields the 9,9,10-trifluoroanthracenonium ion and the corresponding halogen derivatives, including polyfluorinated analogues[23,24] (Scheme 4).

Scheme 4



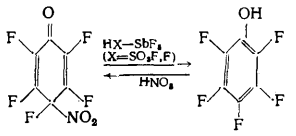
The predominance of the 1-X-9,9,10-trifluoroanthracenonium ions (X = F, Cl, Br) over their 4-X-isomers is obviously a consequence of the occurrence in the latter of destabilising interaction between halogen atoms present in the spatially contiguous resonance positions 4 and 10.

3. Protonation of Polyfluorinated Cyclohexadienones

Cyclohexadienones are conjugated bases of hydroxyarenonium ions, and their protonation has long been used to generate the latter. Koptyug et al.[1] have obtained by this method several hydroxyarenonium ions containing an electronegative atom or group (F, Cl, Br, OH, OCH_3, $OCOCH_3$, NO_2) attached to an sp^3-hybridised carbon atom.

This method has been used to generate polyfluorinated arenonium ions containing as geminal substitutents not only fluorine but also other halogen atoms[25-27]. Ions of the latter type simulate intermediate species in the electrophilic *ipso*-halogenation of aromatic polyfluoro-compounds at positions occupied by fluorine atoms. The ability, revealed by these examples, of chlorine and bromine atoms to be retained at an sp^3-hybrid atom of an arenonium ion in a geminal position with respect to a fluorine atom has served as experimental basis for the generation of polyfluorinated arenonium ions by the direct electrophilic halogenation of aromatic polyfluoro-compounds (below).

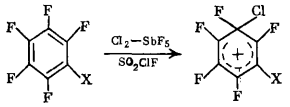
In attempts to generate an arenonium ion containing a nitro-group as substituent located geminally with respect to a fluorine atom, in contrast, pentafluoro-4-nitrocyclohexa-2,5-dien-1-one when dissolved in the systems $HSO_3F-SbF_5-SO_2$ and $HF-SbF_5-SO_2ClF$ is converted into pentafluorophenol, with the dependence of the degree of conversion on the quantity of the pentafluoride corresponding to a stoichiometric ratio of two moles of the latter per mole of the ketone. In the absence of antimony(V) fluoride the reaction does not take place, but nor does protonation of the ketone[28]. Thus introduction of antimony pentafluoride into the system leads to reversal of the *ipso*-nitration of pentafluorophenol[28,29], which may be due to involvement of a nitronium cation in specific complex formation in such systems:



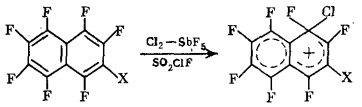
4. Action of Electrophilic Agents on Aromatic Polyfluoro-compounds

Generation of arenonium ions by direct electrophilic attack on aromatic compounds is obviously the most fundamental method for experimental testing of the generally accepted schemes of interaction between aromatic compounds and electrophilic agents. For a long time arenonium ions corresponding to reactions involving addition of an electrophile to an aromatic ring by means of an electronegative heteroatom could not be generated in this way[1]. Success was achieved independently by groups of workers headed by Olah in the USA [30] and by Koptyug in the USSR,[31-33] who used polymethylated aromatic compounds as substrates and strong protic acids as media. These researches, as well as the above results on the fixation of polyfluorinated hydroxyarenonium ions with chlorine and bromine atoms as substituents geminal with respect to a fluorine atom, initiated attempts to generate polyfluorinated arenomium ions by the direct electrophilic halogenation of aromatic polyfluoro-compounds.

The action of molecular chlorine and antimony(V) fluoride on aromatic polyfluoro-compounds in sulphuryl chloride fluoride between −80 and −60 °C forms polyfluorinated 1-chloro-1-fluoroarenonium ions[14,34,35]:

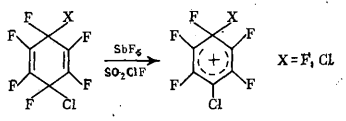


X = F, CH_3, C_6F_5



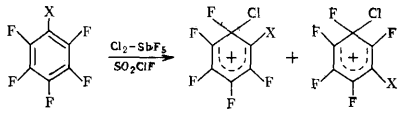
X = F, H, CH_3

With respect to the reaction mechanism, an alternative to direct electrophilic attack on the polyfluoro-aromatic ring would be addition of molecular chlorine on chlorine fluoride followed by reaction between the resulting cyclohexadienes containing a chlorofluoromethylene group and antimony(V) fluroide. Such a possibility is refuted, at least for the chlorination of hexafluorobenzene, by the abstraction of a fluoride anion from the halogenated methylene group when antimony(V) fluoride acts on cyclohexadienes of the above type[14]:



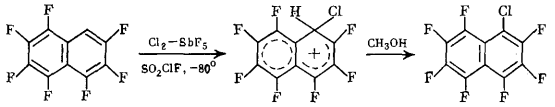
In most of the above cases of the chlorination of aromatic polyfluoro-compounds the orientation of addition of the chlorine cation is consistent with the relative stability of the isomeric polyfluorinated 1,1-difluorobenzenonium and 1,1-difluoronaphthalenonium ions formed by the action of antimony(V) fluoride on polyfluorinated cyclohexadienes or dihydronaphthanlenes (Section III). The only exception is the chlorination of chloro- and bromo-pentafluorobenzenes, with preferential formation of 3-X-1-chloropentafluorobenzenonium ions (X = Cl, Br). Since there are grounds for supposing that at least with polyfluorinated 1-chloro-1-fluorobenzenonium ions, such orientation corresponds to the equilibrium ratios of the isomeric ions (in virtue of the ease of migration of the chlorine atom—Section III), this exception indicates a change in the relative stability of 2- and 3-X-substituted isomers (X = Cl, Br) on passing from 1,1-difluorobenzenonium ions to their 1-chloro-1-fluoro-substituted analogues (Scheme 5). Such a change may be due both to increase in steric strain in the 2-X-isomer with increase in the bulk of the geminal substitutent and to change in the distribution of electron density in the unsaturated portion of the ion under the influence of change in the electronic effect of the substituent at the sp^3-hybridised atom[28,36].

Scheme 5



X = Cl:	33%	67%
X = Br:	20%	80%

Pentafluorobenzene and 1-H-heptafluoronaphthalene are chlorinated under the above conditions at the unsubstituted position. However, whereas in the former case only chloropentafluorobenzene is formed, in the latter a rare example of formation of an arenonium ion corresponding to substitution of hydrogen could be observed:



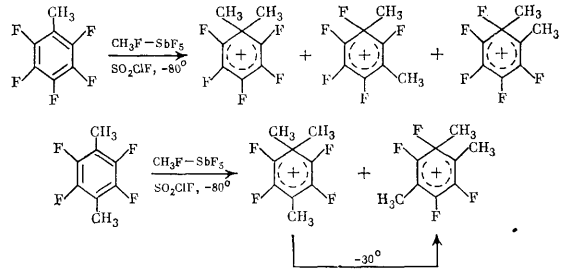
(XXVI)

The chief product of methanolysis of a solution containing this ion is 1-chloroheptafluoronaphthalene. The comparative stability of the ion (XXVI) with respect to detachment of a proton is apparently due to steric hindrance caused by *peri*-interaction when a chlorine atom is situated in the plane of the naphthalene ring system[35].

Attempts have also been made to generate arenonium ions by electrophilic bromination and nitration of aromatic polyfluoro-compounds. Bromination has proved successful with pentafluorotoluene, addition of which to a solution of bromine and antimony(V) fluoride in sulphuryl chloride fluoride at −60 °C forms a 1-X-3 methylpentafluorobenzenonium ion, in which X appears from the chemical shifts of atoms in its immediate vicinity to be a bromine atom[22,36]. However, formation of polyfluorinated arenonium ions could not be detected from the ^{19}F n.m.r. spectra in the action on polyfluorinated

benzenes of nitrating systems containing nitronium fluoroborate or nitrosyl chloride together with fluorosulphuric acid or antimony pentafluoride in sulphur dioxide or sulphuryl chloride fluoride, which recalls the above unsuccessful attempts to generate the 4-hydroxy-1-nitropentafluorobenzenonium ion by protonating the corresponding nitrocyclohexadienone[28].

Scheme 6



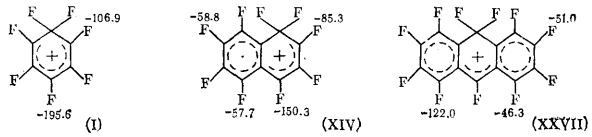
It has recently been discovered that the complex of fluoromethane and antimony(V) fluoride is able to methylate aromatic polyfluoro-compounds at positions occupied by either a fluorine atom or a methyl group, with formation of the corresponding arenonium ions[37]. This method has been used to generate 1,1-, 1,2-, and 1,3-dimethylpentafluorobenzenonium ions in sulphuryl chloride fluoride at −80 °C. The methylation of tetrafluoro-*m*-xylene under similar conditions occurs predominantly at a position occupied by a methyl group, and to a less extent at position 5 occupied by a fluorine atom. With tetrafluoro-*p*-xylene approximately equal quantities of 1,1,4- and 1,2,5-trimethyltetrafluorobenzenonium ions are formed. When the temperature of the solution rises from −80 to −30 °C, the ion containing two geminal methyl groups isomerises with migration of one of them to an adjacent position (Scheme 6).

III. PROPERTIES OF POLYFLUORINATED ARENONIUM IONS

1. Nuclear Magnetic Resonance Spectra and Structure

A most important experimental advance making a considerable contribution to the development of research on polyfluorinated carbocations and on arenonium ions in particular is the possibility of using ^{19}F n.m.r. spectroscopy to detect the formation and study the electronic structure of these species. The great sensitivity of the degree of shielding of fluorine nuclei to structural characteristics of a molecule, producing a change in the chemical shifts of fluorine atoms δ_F over a range of $\sim 10^{-8}$, makes this method a powerful tool for determining the structure of molecules containing fluorine. Furthermore, the predominantly π-electronic character of the variation in shielding of fluorine atoms in series of structurally similar unsaturated compounds makes it theorectically possible to use δ_F values to characterise the influence of structural factors, in particular of substituents quite remote from the given fluorine atom, on the π-electron density distribution. The spin–spin coupling constants between fluorine nuclei are also extremely informative.

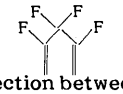
Despite the admittedly approximate character of such an approach, there are grounds for supposing that it gives a qualitatively correct picture of the dependence of the delocalisation of positive charge in polyfluorinated carbocations on their structure. This is indicated, for example, by the decrease in $\Delta\delta_F$ in the series of arenonium ions[14,22,23]



(I) (XIV) (XXVII)

i.e. with gradual increase in extent of the π-electron system (here $\Delta\delta_F$ is the chemical shift of a fluorine atom in the arenonium ion relative to the corresponding fluorine atom in the polyfluoroaromatic precursor, which in this case corresponds to formal removal of one of the geminal fluorine atoms as a cation). The relations between the $\Delta\delta_F$ values for different fluorine atoms in each of these arenonium ions correspond qualitatively with quantum-chemical calculations of the distribution of π-electron density in fluorine-containing arenonium ions[38]. Finally, the $\Delta\delta$ values for fluorine atoms and the carbon atoms to which they are attached in these three ions vary in parallel, in conformity with the equation $\Delta\delta_C = 0.135\,\Delta\delta_F$. Such a correlation apparently indicates that the ratio between the fractional charges on carbon and fluorine atoms remains approximately constant for a given cyclic C–F group, despite variation within wide limits in the degree of delocalisation of the charge[39].

An analysis[40] of $\Delta\delta_F$ values# in a series of arenonium ions generated by protonation of partly fluorinated benzenes[4,7] leads to the conclusion that accumulation of fluorine atoms in the unsaturated part of the ion is apparently accompanied by a redistribution of electron density involving increase in the electron deficiency of the *para*-position but diminution in the deficiency at the *ortho*-positions. Comparison of $\Delta\delta_F$ values for protonated pentafluorobenzene[7] and for the ion (I)[14] shows that replacement of hydrogen by fluorine atoms at an sp^3-hybridised site leads to further increase in the fractional positive charge at the *para*-position, so that the π-electronic structure of ion (I) can be represented to a first approximation by the limiting structure



(B)

The existence of a connection between $\Delta\delta_F$ values of the type of π-electron density distribution reveals the tempting prospect

These tendencies are supported by quantum-chemical calculations[38].

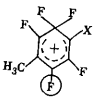
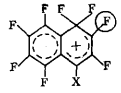
The existence of a connection between $\Delta\delta_F$ values and the type of π-electron density distribution reveals the tempting prospect of elucidating the relations between the electronic effects of substituents. The Table gives values of $\Delta\delta_F$ for series of polyfluorinated arenonium ions differing in the nature of a substituent in a given position. Inspection of these data indicates that the ratio of the $\Delta\delta_F$ values for structurally similar polyfluorinated arenonium and hydroxyarenonium ions is consistent with the generally accepted relation between the electron-donor resonance effects of the hydroxy-group and the fluroine atom. Yet the dependence of $\Delta\delta_F$ for an *o*-fluorine atom in the cyclohexadienyl fragment on the nature of the substitutent X in series of 4-X-hexafluorobenzenonium (X = F, Cl), 4-X-2,3,5,6-tetrafluorobenzenonium (X = F, Cl, Br, H), and 4-X-octafluoronaphthalen-1-onium (X = F, Cl, H)

This analysis is based on an assignment of signals, somewhat different from that of Ref.7, in the ^{19}F n.m.r. spectra of several of the ions.

ions conforms to electron-donor effects of halogens located in the resonance *para*-position diminishing on the whole in the sequence Br > Cl > F.[13,17,20]

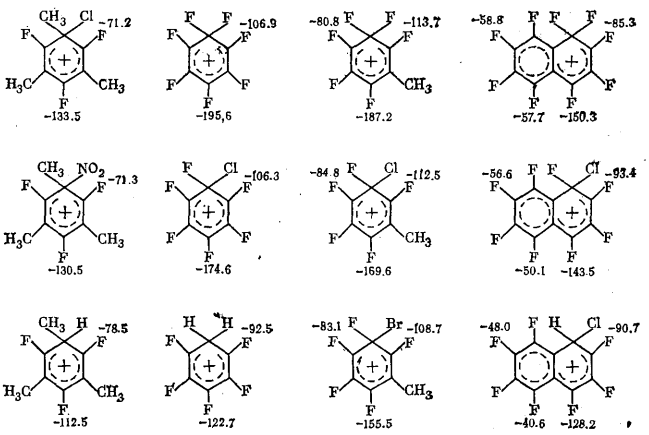
The same laws are revealed by a comparison of $\Delta\delta_F$ values for *p*-fluorine atoms in the cyclohexadienyl fragment of 2-X-hexafluorobenzenonium (X = F, Cl, Br),[13,16] 2-X-5-R-pentafluorobenzenonium (R = CH_3: X = F, Cl, Br; R = H: X = F, Cl, Br, H),[15] and 2-X-octafluoronaphthalen-1-onium (X = F, Cl, Br)[13,17] ions. In 2-X-substituted benzenonium ions, however, substituents X located in resonance positions have different effects on $\Delta\delta_F$ for chlorine atoms in the other two resonance positions, *para* and *ortho*. As the electronic structure of polyfluorinated benzenonium ions closely resembles a limiting structure of type (B), it may be supposed that the relation between the π-electronic effects of substituents X should be evident in the influence of the nature of X on the value of $\Delta\delta_F$ for the *para*-fluorine atom, not for the fluorine atom located in the other *ortho*-position, especially as it coincides qualitatively with the effect of *p*-X-substituents on the shielding of the fluorine atoms in other resonance positions in 4-X-hexafluorobenzenonium[13] and 4-X-2,3,5,6-tetrafluorobenzenonium[20] ions, as well as polyfluorinated arylmethyl cations[41].

Values of $\Delta\delta_F$ for polyfluorinated arenonium ions[15,20,22,25] (for the circled fluorine atom in each formula).

Arenonium ion	X	$\Delta\delta_F$, ppm	Arenonium ion	X	$\Delta\delta_F$, ppm
	F	−106.9		F	−187.2
	Cl	−88.5		Cl	−170.5
	OH	−64.2		Br	−164.7
	H	−96.3			
	F	−92.5		H	−185.6
	Cl	−84.8		F	−186.8
	Br	−81.7		Cl	−170.8
	H	−89.1		Br	−164.8
	F	−85.3		F	−106.9
	Cl	−71.0		Cl	−93.7
	OH	−59.8		Br	−89.6
				H	−83.1
	F	−195.6			
	Cl	−173.9			
	Br	−165.7			

It is extremely important whether the sequence Br > Cl > F of variation in the influence of halogen atoms on the shielding of fluorine atoms in resonance positions actually represents the relation between their resonant electron-donor effects (the influence of *p*-halogen atoms in non-fluorinated benzenonium ions on the $\delta_{^{13}C}$ values of ring *ortho*-carbon atoms is characterised by an analogous series[42]. Indeed, although all halogen atoms exert a greater shielding effect than does a hydrogen atom, which corresponds to predominance of the electron-donor resonance component in their total electronic effects, differences in effects of halogen atoms may be connected mainly with their inductive effects[43] (see discussion of these results in Ref. 44). Sufficiently accurate results obtained by quantum-chemical calculations on the ions are necessary to solve this problem. The influence of substituents in non-resonance positions in the unsaturated part of polyfluorinated arenonium ions on the shielding of fluorine atoms in remote resonance positions is represented by the sequence CH_3 > H > Br > Cl > F, which coincides qualitatively with the generally accepted relation between their inductive effects[15].

Scheme 7



Important data have been obtained on the effects of substituents at the sp^3-hybridised site on the distribution of electron density in, and on the stability of, arenonium ions. The laws governing the reactions of aromatic compounds with various electrophiles[45] and also the actual possibility of generating the arenonium ions that are intermediate species in such reactions may depend on this effect. Such information can be obtained in a series of polyfluorinated arenonium ions by comparing $\Delta\delta_F$ values for ions formed by the protonation of pentafluorobenzene[7,20], the protonation, nitration, and halogenation of trifluoromesitylene[5,31], the halogenation of aromatic polyfluoro-compounds[14,33], and the action of antimony(V) fluoride on polyfluorinated cyclohexadienes[15,20,22]. The data in Scheme 7, illustrating the variation in $\Delta\delta_F$ in series of arenonium ions differing in the nature of the geminal substituents, indicate that decrease in electronegativity of a geminal substituent is accompanied by increase in shielding of the $F_{(4)}$ atom in benzenonium or of $F_{(4)}$, $F_{(5)}$, and $F_{(7)}$ atoms in naphthalen-1-onium ions, which apparently represents diminution in the fractional positive charge in the corresponding C−F groups. It is reasonable to expect an accompanying increase in the fractional positive charge at the *ortho*-position and hence the deshielding of *o*-fluorine atoms. This does actually occur in a series of benzenonium ions generated from trifluoromesitylene. Analogous changes are observed in the ^{13}C n.m.r. spectra of polymethylated benzenonium ions differing in the nature of substitutents at the sp^3-hybridised site[45]. In the remaining series, however, no unambiguous correspondence is observed between variation in $\Delta\delta_F$ for an *o*-fluorine atom and the electronegativity of a substituent at an sp^3-hybrid site. The apparent reason is that changes in $\Delta\delta_F$ observed for *o*-fluorine atoms are largely due to variation in the shielding effect of geminal substituents that is transmitted directly through space. Analogous laws are observed with variation in the nature of geminal substituents in polyfluorinated hydroxyarenonium ions[26].

The $\Delta\delta_F$ values for fluorine atoms at non-resonance positions in the unsaturated part of arenonium ions and also at the sp^3-hybridised site apparently do not reflect the character of the distribution of positive charge. It is sufficient to mention that the signals of geminal fluorine atoms are displaced upfield on passing from polyfluorinated dihydro-aromatic compounds to the corresponding polyfluorinated

arenonium ions[13], which may be due to change specific to this process in the so called van der Waals contribution to the shielding constant[46]. Fluorine atoms at non-resonance positions in the unsaturated part of ions are apparently subject to the deshielding influence of fluorine atoms at neighbouring resonance positions, which bear considerable fractions of the positive charge. This is most likely due to a downfield shift in the signals of fluorine atoms at non-resonance positions relative to the corresponding signals in the ^{19}F n.m.r. spectra of the precursors[13]. An analogous explanation was given for the mutually deshielding influence of *peri*-fluorine atoms in polyfluorinated anthracenonium ions[23].

Even in the early work on the generation of polyfluorinated arenonium ions by the protonation of polyfluorobenzenes[4-6], and later by the action of antimony(V) fluoride on polyfluorinated cyclohexadienes or dihydronaphthalenes[12,13], it had already been shown that *o*- and *p*-fluorine atoms in a cyclohexadienyl fragment are characterised by unusually large absolute values of the spin–spin coupling constants between them, far exceeding those of J_{FF} for similarly oriented fluorine atoms in neutral compounds[47]. This phenomenon was interpreted qualitatively[13], in view of the close similarity of the π-electron system to a limiting structure of type (B), on the basis of effective interaction between the *o*- and *p*-fluorine atoms by a mechanism of conjugation.

From analogous considerations a similar increase in J_{FF} values in polyfluorinated naphthalenonium and anthracenonium ions relative to neutral compounds may be expected for the interaction between fluorine atoms in other resonance positions. In fact values of $J^{5,7}_{FF} \cong 50$ Hz are observed for naphthalene-1-onium ions[13], $J^{2,4}_{FF}$ 35–40 Hz for anthracen-9-onium ions[23], and $J_{FF} = 20-25$ Hz for the interaction of $F_{(2)}$ and $F_{(4)}$ with $F_{(5)}$ and $F_{(7)}$ in naphthalen-1-onium ions[18]. It is significant that the interaction between the spatially contiguous $F_{(3)}$ and $F_{(4)}$ atoms in polyfluorinated benzenonium ions corresponds to values of $J^{3,4}_{FF} = 25-30$ Hz only slightly exceeding those of J^{ortho}_{FF} for neutral fluoro-aromatic compounds[47], whereas the interaction of $F_{(2)}$ with $F_{(3)}$ is characterised by values $J^{2,3}_{FF} = 4-6$ Hz typical of the interaction of vicinal fluorine atoms located at a double bond in a cycloalkene[48], which is consistent with the close similarity of the cyclohexadienyl fragment in a polyfluorinated arenonium ion to the structure (B).

The above generalisations suggest that values of J_{FF} for interaction between fluorine atoms in resonance positions should be extremely sensitive to the type of the delocalisation of positive charge in arenonium ions. In conformity with this a parallelism in the variation of J_{FF} values and chemical shifts of the corresponding fluorine atoms is observed for polyfluorinated arenonium ions[13,23] and also the related arylmethyl cations[41]. From this point of view it is reasonable that the interaction of *peri*-fluorine atoms in naphthalen-1-onium and anthracene-9-onium ions corresponds to values of $J_{FF} = 130-150$ Hz,[13,23] since in neutral derivatives of naphthalene and anthracene such interaction is characterised by values of 60–80 Hz.[49,50] When a hydroxy-group, which exerts a stronger electron-donor effect than does a fluorine atom, is introduced into a resonance position in a polyfluorinated benzenonium or naphthalenonium ion, values of J_{FF} for interaction between fluorine atoms involved in resonance charge delocalisation decrease significantly, as is to be expected[27].

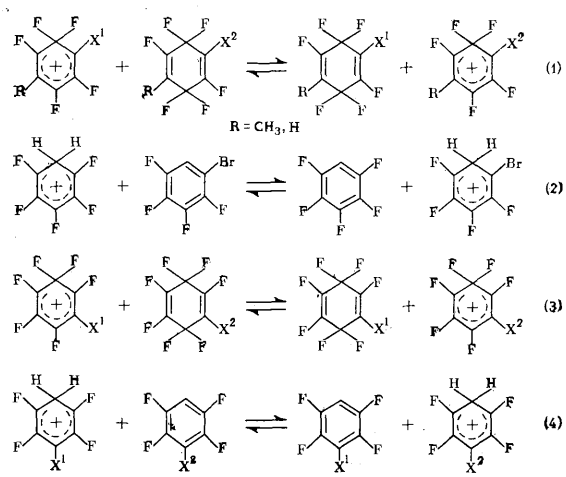
All the results at present available show that the possibility of parallel application of ^{19}F and ^{13}C n.m.r. spectroscopy makes polyfluorinated arenonium ions, and more generally polyfluorinated carbocations of various structural types, extremely interesting subjects for investigation. Detailed study of the dependence of the electronic structure of carbocations on their molecular structure and in particular elucidation of the relations between the electronic effects of substituents become theoretically possible. It may be supposed that, in contrast to the established practice of assessing these relations from the influence of substituents on the relative stability of carbocations or from their rate of formation in solution, such an approach will yield a picture uncomplicated by solvation interactions. The most reliable information can apparently be obtained from a combination of spectral data with results of quantum-chemical calculations.

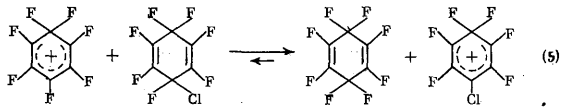
2. Equilibrium Proportions of Polyfluorinated Arenonium Ions and the Stabilising Influence of Substituents

Elucidation of the factors governing the relation between the relative stability of carbocations and their structure is of decisive importance for study of the mechanism of many reactions involving intermediate formation of species of this type. When applied to arenonium ions, this general task becomes the particular problem of establishing a theory of the influence of substituents on the rate and the orientation of reactions of aromatic compounds with electrophilic agents. Polyfluorinated arenonium ions are no exception in this respect, since a considerable volume of data have now accumulated on orientation in electrophilic reactions of aromatic polyfluoro-compounds of two main types—substitution of a hydrogen atom and addition[3,16,51-63].

Although papers on the generation of polyfluorinated arenonium ions contain numerous data on the equilibrium proportions of isomeric ions of this type, they cannot provide information on the relative stabilising effects of substituents at individual positions, since the isomeric ions differ in the nature of substituents at more than one position. In some cases these relations can be assessed from a comparison of the conditions of protonation of the corresponding fluorinated benzenes (Section II). The structure of the resulting benzenonium ions indicates that the *para*-position of a fluorine atom is most favourable to the stability of the ion, whereas the *meta*-position provides the greatest destabilising effect. These results are consistent with quantum-chemical calculations predicting that carbocations with fluorine atoms in resonance positions will be more stable than isomers having a different arrangement of the same substituents[54,55].

Scheme 8





(5)

The traditional approach to elucidating the relative stabilising effects of substituents at individual positions in carbocations is to study the dependence of the equilibrium formation constants of the ions fron neutral precursors on the nature of the substituents[56]. Among polyfluorinated arenonium ions such an approach has been adopted for the equilibrium systems in Scheme 8, formed by the action of a deficiency of a Lewis or a protic acid (depending on the mode of regeneration) on a mixture of equivalent quantities of two precursors[15,20].

The positions of equilibrium in systems (1) and (2) indicate that the stabilising effect of *ortho*-substitutents diminishes the sequence $CH_3 > Br > Cl > H > F$. Similarly, series (3) gives the stability sequence of benzenonium ions with different *meta*-substituents $CH_3 > H > Br > Cl > F$.[15] Relations established in series (4) correspond to variation in the stabilising influence of *para*-substituents in the sequence $CH_3 > F > Br > Cl > H$.[15]

It must be noted that the attempt[20] to assess the relative stabilising effects of *p*-fluorine and *p*-chlorine atoms in corresponding 4-X-hexafluorobenzenonium ions from equilibrium constants in system (5) (with simultaneous generation of the ions by the action of antimony(V) fluoride on a mixture of two cyclohexadienes) gave a relation between chlorine and fluorine opposited to that found for series (4). However, this apparently does not represent the true relation between the stabilising effects of *p*-chlorine and *p*-fluorine atoms in polyfluorinated arenonium ions, since the requirement that structural differences should be remote from the bond undergoing rupture in the precursors is not met[57]. In such a situation differences in the equilibrium position may be due to structural features not so much of the ions as of their precursors, so that the observed relations cannot be interpreted in terms of effects of substituents in the ions themselves. The decisive role may be played by differences in steric stress or in strength of the carbon–fluorine bond in difluoro- and chlorofluoro-methylene groups of the cyclohexadiene precursors (see Refs.58 and 59 for the effect of the accumulation of geminal fluorine atoms on the carbon–fluorine bond strength).

Nevertheless, it must borne in mind that the relative stabilising effects of halogen atoms are apparently very sensitive to other structural characteristics of arenonium ions. Thus in series (1) differences in the relative stability of *o*-bromo- and *o*-fluoro-ions correspond to equilibrium constants of concurrent generation of the ions $K \geq 300$. In the concurrent protonation of 1-bromo-2,3,4,5-tetrafluorobenzene and pentafluorobenzene (system 2) the difference is characterised by the value $K = 1.5$ [15] with preservation of the qualitative relation between the stabilising effects of *o*-bromine and *o*-fluorine atoms.

In view of the correspondence between the influence of substituents on the relative stability of cations and on the shielding of a fluorine atom in a resonance position remote from the substituents in 4-fluorinated di- and tri-phenylmethyl cations and related zwitterions[60,61], considerable interest attaches to a comparison of the above data on the influence of substituents on the ^{19}F n.m.r. spectra and on the relative stability of polyfluorinated arenonium ions. In series (3) the ions exhibit a complete qualitative correspondence between the influence of 3-substituents on $\Delta\delta_F$ for the $F_{(6)}$ atom and on the relative stability of the ion, the relations in both cases being consistent with the generally accepted sequence of variation in inductive effects in the series of substituents[15]. In series (1) and (2) there is similarly a qualitative correspondence between the effects of *o*-halogen or *o*-hydrogen atoms in the benzenonium ion on $\Delta\delta_F$ for a *p*-fluorine atom and on the relative stability of the ion. Such parallelism is characteristic of arenonium ions formed by the protonation of 1-X-2,3,4,5-tetrafluorobenzenes (X = F, Br).[15] If the variation in shielding effect of substituents in this sequence actually represents their relative electron-donor resonance effects (other possible reasons for the observed relationship with halogen atoms have been given in this Section), it may be supposed that these effects are mainly responsible also for the observed variation in stabilising influence.

It is noteworthy that such correspondence does not exist with *p*-substituents and an *o*-fluorine atom acting as indicator: although the shielding sequence of *p*-halogen and *p*-hydrogen atoms for series (4) coincides qualitatively with that of the *same* substituents located at *ortho*-positions in series (1) and (2), the stabilising effects of halogen atoms in series (4) vary in the different sequence $F > Br > Cl$.[20] The absence of such parallelism may mean that for the given substituents the order of variation in electron-donor resonance effect does not coincide with that in stabilising effect. The main contribution to the relation between the stabilising effects of halogen atoms as substituents bearing considerable fractions of the positive charge may then be made by their solvation interaction with surrounding species[20] (cf. discussion in Ref.62 on the solvation of carbocations). Such solvation effects may also be responsible to some extent for the fact that, as already noted[1,63], halogenated arenonium ions appear more stable in superacid media than could be expected from the effects of halogen atoms in the usual reactions of halogenobenzenes with electrophilic reagents.

In view of the above considerations it is noteworthy that resuits on the shielding and stabilising effects of *p*-halogen atoms in benzyl cations related to arenonium ions indicate that the parallelism between these effects may break down when hydrogen atoms are completely replaced by fluorine atoms[41]. With such modification the shielding effects of halogen atoms are reversed ($F > Cl > Br > H$ for αα-difluoro-*p*-halogenobenzyl cations[64] and $Br > Cl > F > H$ for hexafluoro-*p*-halogenobenzyl cations[41]), while their stabilising effects merely level off. This also may indicate that some factor other than the electronic effect of the substituent may make a significant contribution to the stabilising influence of *p*-halogen atoms, with the qualitative sequence of *p*-substituents apparently maintained with respect to this component of the stabilising effect on passing from αα-difluoro- to hexafluoro-*p*-halogenated benzyl cations[20]. A significant influence of solvation on the relative stabilising effects of halogen atoms may be indicated also by the diminution in stability of benzyl cations in the sequence of *p*-substituents $H > F > Cl$ suggested by the ionisation potentials of the benzyl radicals[65], whereas in antimony(V) fluoride with sulphuryl chloride fluoride *p*-halogen atoms are more strongly stabilising substituents of αα-difluorobenzyl cations than is a hydrogen atom[20].

In series (1), (3), and (4) in Scheme 8 polyfluorinated arenonium ions are considerably more strongly stabilised by a methyl group than by halogen atoms. With *meta*-orientation (series 3) this corresponds to the position occupied by methyl in the shielding sequence of substituents; with *ortho*- or *para*-orientation of this substituent—series (1) and (4)—such correspondence is absent. This apparently indicates that both shielding and stabilising effects of a methyl group differ significantly in nature from the corresponding effects of halogen atoms when these substituents are located in resonance positions.

The relations between the stabilising effects of substituents at individual positions in polyfluorinated arenonium ions revealed in series (1)–(4) provide an approach to an understanding of certain factors predetermining the equilibrium isomeric composition of ions generated by the action of antimony(V) fluoride on polyfluorinated cyclohexadienes (Section II). For example, the formation of *m*-methyl isomers in series (1) in no way means that *meta*-orientation is preferable to *ortho*- or *para*-orientation, but rather is due to a tendency to avoid the destabilising influence of a *m*-halogen atom. An indication of this is that, when a hydrogen atom and a methyl group are present in the same series as substituents other than fluorine atoms, the latter occupies an *ortho*- not a *meta*-position in the corresponding ion. On the other hand, the obvious reason for the strongly marked tendency of a fluorine atom to occupy the *para*-position is that only then is it a stronger stabilising substituent than other halogen atoms.

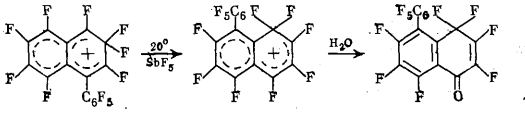
A method of concurrent generation has provided data on the influence of the accumulation of fluorine atoms on the relative stability of 9,9,10-trifluoroanthracenonium ions[66]. Introduction of a fluorine atom at position 2 somewhat stabilises the ion, whereas simultaneous introduction of fluorine atoms at positions 1 and 4 leads to its destabilisation. Further decrease in relative stability occurs on the complete replacement of hydrogen by fluorine atoms, initially in one and then in both benzene rings of the anthracene-9-onium ion. All these changes are consistent with the influence of the structural modifications on the shielding of fluorine atoms, apparently representing a redistribution of π-electron density[23].

3. Isomerisation of Polyfluorinated Arenonium Ions

An urgent task in the investigation of arenonium ions is to study their isomerisation, the importance of which extends far beyond the chemistry of such ions[1,67]. Polyfluorinated arenonium ions undergo several types of isomerisation. In Section II we have already mentioned their reversible isomerisation, involving successive addition and detachment of a fluoride anion with intermediate formation of polyfluorinated dihydro-aromatic compounds. Isomeric polyfluorinated naphthalenonium ions containing the sp^3-hybridised site and the substituent other than fluorine in different rings undergo analogous interconversions. These processes take place under appreciably more severe conditions than does isomerisation in which the positions of the substituent and the sp^3-hybridised site vary within the same ring. The reason is obviously that addition of a fluoride anion to the benzene ring of a naphthalenonium ion entails complete loss of aromaticity[17–19] (Scheme 9).

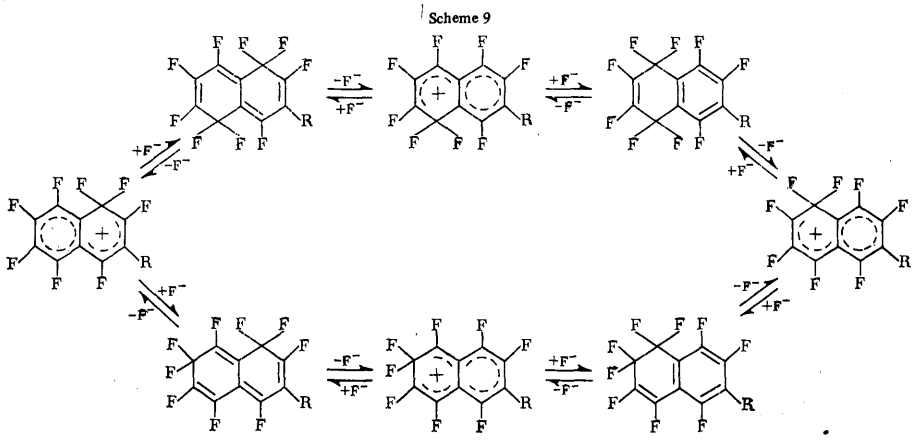
The investigation of such processes broadens significantly our ideas on the thermodynamics of polyfluorinated naphthalenonium ions. Thus 6-X-octafluoronaphthalen-1-onium ions in which X = CH_3, H are completely converted into the corresponding 3-X-isomers[17,18], but with X = C_6F_5 the equilibrium ratio 3-X : 6-X = 2 : 1 is established[19]. When X = Cl, Br, the substituent is also located preferentially at a β-position in the cyclohexadienyl fragment—not in the benzene ring—of the polyfluorinated naphthalene-1-onium ion[17]. In all these cases transfer of the substituent X from the benzene to the cyclohexadienyl ring is accompanied by the reverse migration of the fluorine atom, which, situated *ortho* or *meta* in the cyclohexadienyl fragment, is the most destabilising of the substituents examined (see data in subsection 2 on relative stabilising effects of substituents at individual positions in polyfluorinated benzenonium ions). Therefore the thermodynamic relations displaced in these examples can obviously be linked with the greater effect, on the relative stability of the ion, of substituents present in the cyclohexadienyl fragment than of those located in the benzene ring.

Somewhat different relations hold when a substituent other than fluoro occupies an α-position in a polyfluorinated naphthalenonium ion. For example, the perfluoro-4-phenylnaphthalen-2-onium ion passes into the perfluoro-8-phenylnaphthalen-1-onium ion, as is indicated by the isolation of dodecafluoro-1,4-dihydro-5-phenylnaphthalen-1-one from the products of hydrolysis of the reaction mixture[21]:



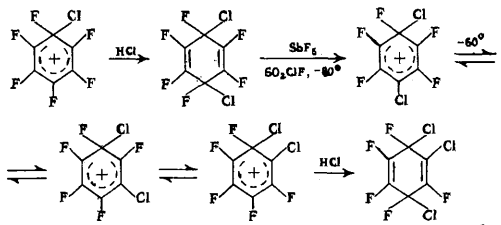
The first example of migration of a geminal substitutent in polyfluorinated arenonium ions was observed in those formed by addition of a proton to an unsubstituted carbon atom in fluorobenzene, *o*- and *p*-difluorobenzenes, and also 1,2,3,4-tetrafluorobenzene. These processes involve those isomers between which transition can be achieved only by 1,2-migration of a hydrogen atom from one unsubstituted ring position to another. The temperature conditions under which changes due to these intramolecular processes are detected in the n.m.r. spectra indicate that 4-mono- and 3,4-di-fluorobenzenonium ions are considerably more stable than their isomers[7]. Such a substantial difference in ease of occurrence of individual stages in 1,2-migration of a hydrogen atom as occurs with protonated fluorobenzenes is not observed with toluene and *o*-oxylene. This is because differences in energy between isomeric benzenonium ions distinguished by the position of a methyl group in the unsaturated part of the ion are not so large as with isomers differing in the position of a fluorine atom[7].

Scheme 9



Recent years have seen the discovery of isomeric changes in arenonium ions involving migration of various electronegative heteroatomic groups corresponding to active attacking species in electrophilic reactions of aromatic compounds[1,68]. A series of polyfluorinated arenonium ions have undergone isomerisation as a result of migration of a chlorine atom, which, unlike the proton in the above examples, is able to pass from one to another geminal position relative to a fluorine atom. Thus the 1,4-dichloropentafluorobezenonium ion, generated as in Scheme 10, is converted with rise in temperature of the solution from −80 to −60 °C into a mixture of 1,4-, 1,3-, and 1,2-dichloropentafluorobenzenonium ions (5%, 62%, and 33% respectively). Treatment of this mixture with hydrogen chloride yields 1,3,6-trichloropentafluorocyclohexa-1,4-diene[69] (Scheme 10).

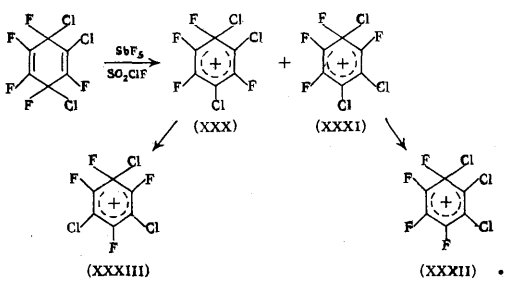
Scheme 10



(XXVIII) (XXIX)

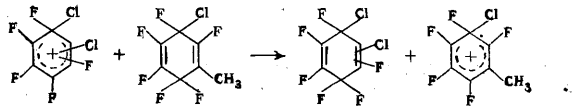
Reaction of this diene with antimony(V) fluoride in sulphuryl chloride fluoride at −90 °C yields not only the primary products of detachment of a fluoride anion—1,2,4- and 1,3,4-trichlorotetrafluorobenzenonium ions (XXX) and (XXXI)—but also two other ions, the 1,2,3- and 1,3,5-trichlorotetrafluorobenzenonium ions (XXXII) and (XXXII), having a different relative arrangement of chlorine atoms than in the original diene (Scheme 11). With rise in temperature to −70 °C the signals of the initially formed ions (XXX) and (XXXI) disappear from the ^{19}F n.m.r. spectrum of the solution, and only those of their isomerisation products (XXXII) and (XXXIII) in the proportions 1 : 1.3 remain. It is interesting that these two ions are extremely stable: right up to −30 °C they are not converted into isomers having two fluorine atoms at the sp^3-hybridised site[36], in contrast to other polyfluorinated benzenonium ions containing chlorofluoromethylene as geminal group (Section II). This may be due to improvement in the stability of polyfluorinated arenonium ions relative to their cyclohexadiene precursors as fluorine atoms in the unsaturated part of the ion are replaced by chlorine atoms, with a consequent raising of the energy barrier to addition of a fluoride anion at resonance positions in the arenonium ion.

Scheme 11



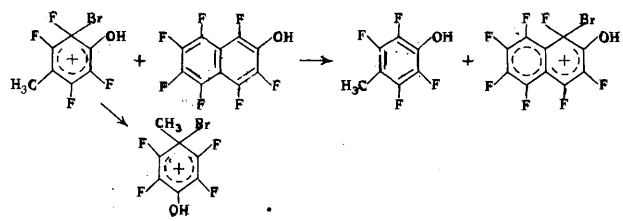
(XXXIII) (XXXII)

In the above cases isomerisation apparently occurs by intramolecular migration of a chlorine atom. This is indicated by absence of transfer of chlorine to pentafluorotoluene or pentafluorobenzene added to the reaction medium under conditions for isomerisation of the dichloropentafluoro- and trichlorotetrafluoro-benzenonium ions, although both additives are chlorinated by a mixture of molecular chlorine and antimony(V) fluoride in sulphuryl chloride fluoride, with formation respectively of the 1-chloro-3-methylpentafluorobenzenonium ion[14] and chloropentafluorobenzene[35]. The absence of such transfer to added pentafluorotoluene cannot be attributed to displacement of the equilibrium towards the ions (XXVIII)–(XXXIII), since addition of 3-chloro-1-methylhexafluorocyclohexa-1,4-diene to a solution containing the ions (XXVIII) and (XXIX) shifts the equilibrium towards an ion that is a chlorination product of pentafluorotoluene[69]:

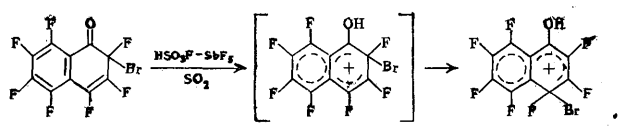


This result was to be expected from the relations elucidated[15] between the stabilising effects of halogen atoms and the methyl group as substituents in polyfluorinated arenonium ions.

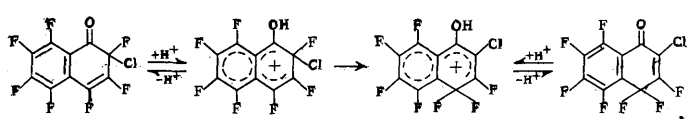
In contrast to this, conversion of the 1-bromo-1,3,4,6-tetrafluoro-2-hydroxy-5-methylbenzenonium ion into the 1-bromo-4-hydroxy-1-methyl isomer occurs most probably by intermolecular migration of the bromine atom, since addition of heptafluoro-2-naphthol yields the 1-bromoheptafluoro-2-hydroxynaphthalen-1-onium ion and tetrafluoro-*p*-cresol[27]:



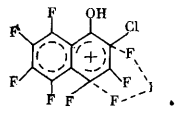
In an attempt to protonate 2-bromoheptafluoro-1,2-dihydronaphthanlen -1-one in the HSO_3F–SbF_5–SO_2ClF system between −70 and −40 °C formation of the corresponding 1-hydroxynaphthalen-2-onium ion could not be observed at all. Its isomer—the 1-bromoheptafluoro-4-hydroxynaphthalen-1-onium ion—was detected, undoubtedly as a consequence both of the greater stability of the naphthalen-1-onium than of the naphthalen-2-onium ion and of the ease of migration of the bromine atom[27]:



It is interesting that the 2-chloroheptafluoro-1-hydroxynaphthalen-2-onium ion, corresponding to protonation of 2-chloroheptafluoro-1,2-dihydronaphthanlen-1-one, could be detected. This also isomerises into the more stable 4-hydroxynaphthalen-1-onium ion, not by migration of the chlorine atom, as might have been expected from the relative tendencies of chloro- and fluoro-aromatic compounds to undergo isomerisation[67], but formally by transfer of a fluorine atom[27]:



This process is due to isomerisation either of the ion or of the precursor in equilibrium with it, apparently by a specific mechanism[70] involving hydrogen fluoride and a cyclic transition state of the type



(C)

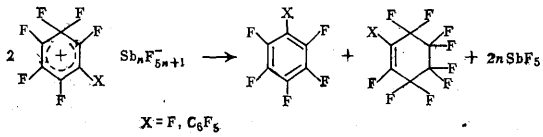
Thus known processes involving the isomerisation of polyfluorinated arenonium ions are at present limited to the transfer of hydrogen, chlorine, and bromine atoms. Apparently only in the case of the chlorine atom does intramolecular migraton occur from one position occupied by a fluorine atom to another. Determination of the relative tendencies of various groups to migrate for arenonium ions in the broad sense is important for interpreting the factors responsible for the orientation observed in reactions of aromatic compounds with electrophilic agents.

The most thoroughly studied reactions of this type in polyfluoro-aromatic compounds are those with nitrating agents, during which attack by the nitronium cation can be directed either at an unsaturated position in the aromatic ring or at those occupied by various substituents, including fluoro[3]. In this connection special interest attaches to the ability of a nitro-group to migrate "around the framework of the polyfluorinated molecule", a problem whose solution is prevented by the lack of methods for generating stable arenonium ions containing geminal fluorine atom and nitro-group at the sp^3-hybridised site. The only known fluorine-containing arenonium ion corresponding to addition of a nitronium cation to the aromatic ring—the 2,4,6,-trifluoro-1,3,5-trimethyl-1-nitrobenzenonium ion—exhibits no tendency to undergo rearrangement, whereas its completely methylated analogue—the hexamethyl-1-nitrobenzenonium ion—readily automerises as a result of intramolecular migration of the nitro-group[30]. The absence of rearrangement in the former case is apparently due to the significantly lower stability of the isomer corresponding to addition of the nitronium cation to trifluoromesitylene at a position occupied by a fluorine atom: this results in a considerably lower activation barrier to movement of the nitro-group from a position occupied by a methyl group to a neighbouring position.

4. Transformations of Polyfluorinated Arenonium Ions in the presence of or in Antimony(V) Fluoride

Progress made during recent years in the development of methods for generating arenonium ions under "long life" conditions not only has extended the possibility of solving various theoretical problems associated with the properties of these species but has also enabled their synthetic utilisation to be envisaged. In this category we can include results obtained in studying the reactions of polyfluorinated arenonium ions in the presence of or in antimony(V) fluoride.

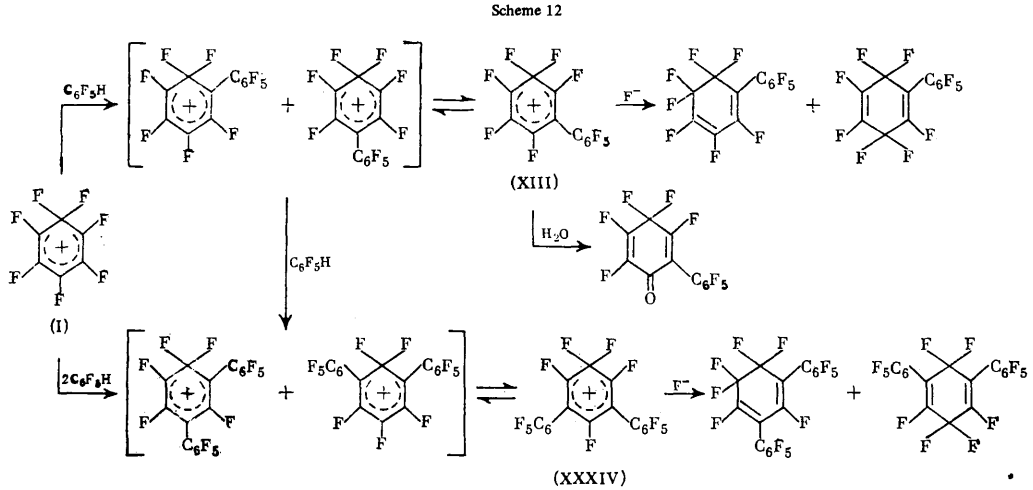
Perhaps the most interesting feature of these reactions is the capacity of polyfluorinated arenonium ions in many cases to undergo aromatisation by formal removal of a fluorine cation from the sp^3-hybridised site. Thus heptafluorobenzenonium hexafluoroantimonate disproportionates in solution to form equal quantities of hexafluorobenzene and decafluorocyclohexene[71]. Perfluoro-3-phenylbenzenonium hexafluoroantimonate undergoes an analogous transformation, but in this case the reaction is apparently complicated by fluorination by antimony(V) fluoride of phenylcyclohexadiene present in equilibrium with the benzenonium ion, so that perfluorophenylcyclohexene predominates over perfluorobiphenyl among the reaction products[19]:



X = F, C_6F_5

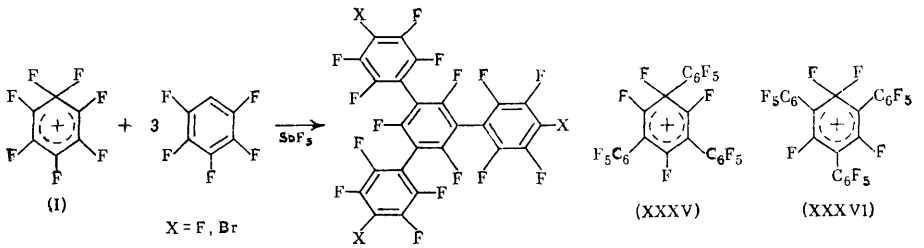
Aromatisation of polyfluorinated arenonium ions has been observed also when they react with partly fluorinated aromatic compounds in antimony(V) fluoride. Reaction of the ion (I) with one equivalent of pentafluorobenzene yields the perfluoro-3-phenylbenzenonium ion (XIII) [Scheme 12]. A mechanism has been suggested involving electrophilic attack on pentafluorobenzene by the most electrophilic centre in the heptafluorobenzenonium ion—the *p*-carbon atom—followed by a series of interconversions of polyfluorinated phenylated cyclohexadienes and benzenonium ions[19]. Addition of a second equivalent of pentafluorobenzene to (XIII) or interaction of (I) with two equivalents of pentafluorobenzene yields the perfluoro-3,5-diphenylbenzenonium ion (XXXIV).

Scheme 12



(XXXIV)

Scheme 13



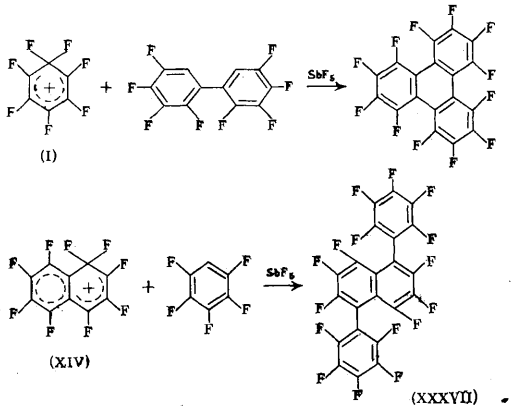
The structure of the latter indicates that the second equivalent probably interacts not with (XIII) but with the perfluoro-2-phenylbenzenonium ion, present in low concentration in equilibrium with (XIII), after which the reaction proceeds by a mechanism similar to that suggested to explain formation of the ion (XIII). Hydrolysis of solutions of salts of arenonium ions generated in this way or their dilution with sulphur dioxide yields polyfluorinated phenylated cyclohexadienones or cyclohexadienes respectively[72].

When the ion (I) is treated with three or more equivalents of pentafluorobenzene in antimony(V) fluoride, formation neither of any arenonium ions containing three or more pentafluorophenyl groups nor of compounds corresponding to hydrolysis of these species or their capture by a fluoride anion can be detected. Furthermore, perfluoro-1,3,5-triphenylbenzene is obtained in yields up to 70%. This apparently means that entry of a third pentafluorophenyl group is immediately followed by rapid aromatisation of the cyclohexadienyl fragment of one of the perfluorophenylbenzenonium ions (XXXV) and (XXXVI), a process distinct from the above disproportionation of the hexafluoroantimonates of the ions (I) and (XIII).

The ion (I) reacts similarly with 1-bromo-2,3,5,6-tetrafluorobenzene. Of the two most probable precursors of a polyfluorinated 1,3,5-triphenylbenzene—ions of types (XXXV) and (XXXVI) (Scheme 13)—the former is prefered, since its structure corresponds to the tendency of the pentafluorophenyl group to occupy a *meta*-position in the unsaturated part of the ion. Furthermore, no aromatisation processes other than the above disproportionation have been observed for benzenonium ions containing two fluorine atoms attached to the sp^3-hybridised carbon atom, which include ions of type (XXXVI).[72]

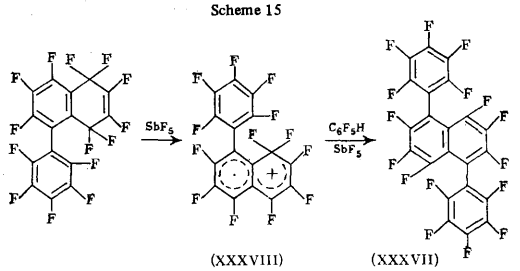
Reactions of this type are obviously of interest as routes for the synthesis of difficultly accessible polyfluorinates polycyclic aromatic compounds. This is illustrated by the syntheses of perfluorotriphenylene from (I) and 2,2',3,3',4,4',5,5'-octafluorobiphenyl[72] and of perfluoro-1,5-diphenylnaphthalene (XXXVII) from the perfluoronaphthalen-1-onium ion (XIV) and pentafluorobenzene[21,73] [Scheme 14].

Scheme 14

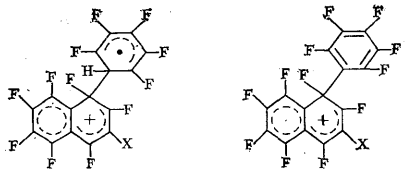


The second reaction apparently involves electrophilic attack on pentafluorobenzene by the 4-carbon atom in (XIV), followed by a series of isomeric conversions of polyfluorinated phenylnaphthalenonium ions yielding the perfluoro-8-phenylnaphthalene-1-onium ion (XXXVIII). This reacts with a second equivalent of pentafluorobenzene to form the compound (XXXVII). The reality of this transformation is confirmed by the formation of (XXXVII) by the action of pentafluorobenzene on the precursor of the ion (XXXVIII)—perfluoro-1,4-dihydro-5-phenylnaphthalene (Section II)—in the presence of antimony(V) fluoride[21] (Scheme 15).

Scheme 15



Those of the isomeric ions in which a fluorine atom and a pentafluorophenyl group are geminal substituents are probably responsible for aromatisation of the cyclohexadienyl fragment in polyfluorinated arenonium ions during the above reactions. This hypothesis has found some support in the formation of polyfluorinated 1-mono- and 1,5-di-phenylnaphthalenes also in the reactions of stable radical-cations of 2-X-heptafluoronaphthalenes (X = F, H, CH_3) with pentafluorobenzene[21] and with tetrafluorobenzenes[74] in antimony(V) fluoride. In terms of the schemes usually employed to describe the oxidative condensation of aromatic compounds involving radical-cations these reactions suggest, in view of the orientation for X = H, CH_3 (cf. data in Section II on relative stabilities of isomeric polyfluorinated arenonium ions containing these substituents), intermediate formation of species of type (XXXIX) and/or (XL), with the former perhaps being converted into the latter[21].



Examples of the reactions of polyfluorinated arenonium ions given in the present Review form only a small fraction of the results illustrating the opening of a new chapter in organic synthesis with the development of methods for generating and studying the properties of stable carbocations. The ensuing possibilities are difficult to overestimate, and at the present time we are witnessing the initial stage of their realisation.

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The Mössbauer Spectroscopy of Tin Halide Complexes with Organophosphorus Ligands

Sh.Sh.Bashkirov, I.Ya.Kuramshin, A.S.Khramov, and A.N.Pudovik

The Mössbauer parameters (the isomer shift δ, the quadrupole splitting ΔE, and the probability of recoilless absorption f') have been analysed for a large number (more than 200) of complexes of mono- and bi-dentate organophosphorus complexes with tetra-alkyltin and alkyltin halides. It is shown that the Mössbauer method can be used to determine the localisation centres of the donor-acceptor bond in complexes of organophosphorus compounds with tin tetrahalides and to determine the geometrical structures of the complexes. It has been observed that the quantities δ, ΔE, and f' for the compounds $[R'R''R'''P(Y)]_{2(1)}SnR_nX_{4-n}$ are definitely influenced by the nature of the substituents in the ligand and in the acceptor. This influence can be described with the aid of the reaction constants of the substituents σ^{ph} and σ^*.
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I. INTRODUCTION

The Mössbauer effect or nuclear gamma resonance (NGR) have been used recently on an extremely wide scale in a wide variety of fields of science and technology. Mössbauer spectroscopy has found the most extensive applications in chemistry: in physical chemistry, in the chemistry of coordination compounds, in nuclear chemistry, etc.[1]

The extensive and effective applications of Mössbauer spectroscopy in chemistry, particularly in the chemistry of organoelemental compounds, are due to the fact that the Mössbauer isotopes ^{57}Fe and ^{119}Sn have come to be most widely used in Mössbauer spectroscopy (these isotopes are relatively readily available and sources based on them are simple to prepare and to use in experiments). On the other hand, as a consequence of the enormous importance of iron- and tin-containing compounds in science and technology, the chemistry of these elements has been studied in extremely great detail. This happy coincidence led to the intensive employment of the Mössbauer effect for studies on organoelemental compounds.

The accumulation of extensive experimental data on Mössbauer spectroscopy during the last twenty years (the effect was discovered by Mössbauer in 1958[2]) entailed the appearance of a whole series of monographs and reviews in which the principles and applications of Mössbauer spectroscopy are described fairly completely[1,3,4]. However, unfortunately none of these publications deals with studies of the class of organoelemental compounds comprising the complexes of tin halides with organophosphorus ligands.

On the other hand, the interest in the coordination compounds of phosphorus is due to the fact that the wide variety of organoelemental compounds containing phosphorus and the unique set of their properties make these substances extremely valuable both for science and for practical purposes. Among organophosphorus compounds (OPC) and their complexes, effective medicinal substances have been found and many OPC are flotation agents, additives to oils, and plasticisers. Coordination compounds of the OPC have found applications in the preparation of materials in various fields (quantum electronics, microelectronics, etc.).

The most important Mössbauer parameters for chemistry are the isomer or chemical shift δ and the quadrupole splitting ΔE, the knowledge of which permits inferences to be drawn about the structure of the electronic valence shell and the geometrical structure of the immediate environment of the Mössbauer atom, about the nature of the chemical bond, etc. Yet another Mössbauer parameter—the probability of recoilless absorption f'—is also of undoubted interest; it permits the study of the dynamic properties of crystals, which depend on the masses of the atoms and on the force constants characterising the interaction between them.

The aim of the present review was to survey the available data on the Mössbauer spectroscopy of tin halide complexes with organophosphorus ligands and to examine the relation between the Mössbauer parameters, the reactivities, and the structures of the compounds. We do not deal with the experimental features of the Mössbauer spectroscopy of ^{119}Sn, which have been described fairly completely elsewhere[1,5-7].

In all cases the isomer shifts, the quadrupole splittings, and the resonance line widths (Γ) are quoted in terms of units of velocity (mm s^{-1}). The isomer shifts are given relative to SnO_2 at room temperature; if the shift is indicated in the original publication relative to another compound, the appropriate recalculation has been made. Since in virtually all studies the accuracy of the determinations of δ, ΔE, and Γ is stated to be in the range $\pm 0.03-0.05$ mm s^{-1}, we shall assume that the experimental error of the determination of these parameters is in this range. The accuracy of the determination is to within ± 0.03. The Mössbauer spectra of the compounds described below have been obtained in the region of liquid nitrogen temperatures (78–90 K) unless otherwise stated.

II. THE ISOMER SHIFT

1. The Influence of the Donor Atom

The isomer or chemical shift is the difference between the energies of the nuclear transitions in the absorbing and emitting nuclei. In the Mössbauer spectra this is manifested

by a shift of the absorption resonance line relative to the emission resonance line (Fig. 1).

In the general case the isomer shift is defined in the following way[1,3,4]:

$$\delta = \frac{4}{5}\pi e^2 z R^2 \frac{\Delta R}{R}\{|\psi(0)|_a^2 - |\psi(0)|_s^2\}, \quad (1)$$

where e is the electronic charge, z the nuclear charge, R the average charge radius of the nucleus, ΔR its change on transition from the ground to the excited state, and $|\psi(0)|_a^2$ and $|\psi(0)|_s^2$ are the electron densities at the nucleus in the absorber and the source respectively. Since the contribution of the inner shells in tin compounds is approximately constant[1,4], δ depends on the population of the valence shell of the Mössbauer atom. Furthermore, theoretical analysis[1,4,8] and numerous experimental results[9-12] showed that in the case of tin(IV) compounds one can neglect to a first approximation the population of the 5p states of the tin atom and the mutual shielding of the s electrons by the p and d electrons.

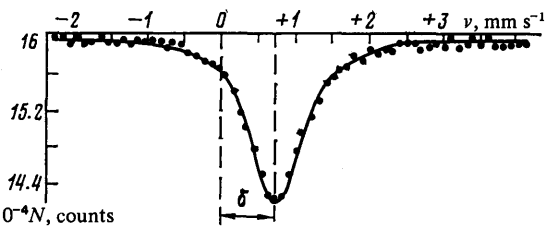


Figure 1. The Mössbauer spectrum of the complex $[(C_2H_5)_2P(S)S]_2SnCl_2$ at 85 K (continuous line—calculation).

Thus the state of the Mössbauer atom in various chemical compounds is determined primarily by the structure of the outer electronic valence shells and the main contribution to δ for tin-containing compounds comes from the difference $|\psi_{5s}(0)|_a^2 - |\psi_{5s}(0)|_s^2$. Consequently the relative change in the population of the valence 5s shells of the tin atom in a series of different absorbers (for a fixed source) can be inferred from the change in δ.

Since $\Delta R/R > 0$ for ^{119}Sn, one can claim unambiguously that, for tin-containing compounds, a large value of δ corresponds to a large population of the 5s shell of the tin atom. Thus if 100% covalent bonding is assumed in α-tin ($\delta = 2.1$ mm s^{-1}), i.e. that the population of the 5s orbital is 1.0–1.2 electrons[5,15,16], and a 50% ionic bond character is assumed for SnF_4 ($\delta = -0.25$ mm s^{-1}),[4] then evidently the closer the value of δ for any tin-containing compound to that for SnF_4, the smaller the population of the 5s shell of the tin atom in the given substance.

Thus the isomer shift permits inferences about the chemical environment of the Mössbauer atom in various compounds. Such analysis is particularly simple for the determination of the valence state of tin. Thus, for bivalent tin, the isomer shift relative to α-tin is greater than zero, while for quadrivalent tin it is less than zero[17]. If the shifts are considered relative to SnO_2 (a generally recognised standard in ^{119}Sn Mössbauer spectroscopy), then $\delta > 2.1$ mm s^{-1} for tin(II) and $\delta < 2.1$ mm s^{-1} for tin(IV). One must note that in certain complexes of the type $LSnCl_3$ the isomer shift ($\delta > 2.1$ mm s^{-1}) does not allow the estimation of the formal valence of tin[18].

Systematic treatment and analysis of the literature data[10-12,19-24] and the authors' own results[25-43], summarised in Tables 1–9, permits the claim that the values of δ for compounds of the type $L_3(L')SnX_4$ and the ratio of the isomer shifts of $L_2(L')SnBr_4$ (δ_{Br}) and $L_2(L')SnCl_4$ (δ_{Cl}) is determined in the first place by the nature of the immediate environment of the tin atom (Table 1) and this makes it possible to use Mössbauer spectroscopy for the determination of the localisation centres of the donor–acceptor bond in complexes of organophosphorus compounds with both tin chloride and tin bromide.

Table 1. The isomer shifts and quadrupole splittings in the Mössbauer spectra of tetra-alkyltin compounds, tetra-aryltin compounds, alkyltin halides, and aryltin halides with mono- and bi-dentate organophosphorus ligands $L_2(L')SnX_4$, $L_2SnR_nX_{4-n}$ ($n = 1,2$), and $LSnR_3Cl$ and of the organotin salts L_2SnX_2 at 78–90 K.[38,40]

No.	L(L′=5–8)	Acceptor	δ, mm s⁻¹		$\left(\frac{\delta_{Br}}{\delta_{Cl}}\right)_{av}$	ΔE, mm s⁻¹		ρ=ΔE/δ		Number of compounds	
			X=Cl	X=Br		X=Cl	X=Br	X=Cl	X=Br	X=Cl	X=Br
1	R′R″R‴P(O)	SnX_4^*	0.24–0.51	0.55–0.65	2.0	0.5–1.6 (*trans*); 0.5*** (*cis*)	0.6–1.11 (*trans*); 0.4 (*cis*)	1.6–3.1	1–1.9	56	22
	»	$SnRX_3$	0.80–1.15	1.00–1.05	1.36	1.99–2.36	2.02–2.31	1.91–2.64	2.02–2.20	10	2
	»	SnR_2X_2	1.20–1.60	1.56	1.09	3.81–4.37	4.40	2.54–3.24	2.81	18	1
	»	SnR_3X	1.29–1.52	—	—	3.07–3.85	—	2.41–2.64	—	9	—
2	R′R″R‴P(S)	SnX_4	0.58–0.71	0.88–1.07	1.4	⩽0.50	⩽0.40	⩽0.95	⩽0.4	21	9
3	R′R″R‴P(Se)	SnX_4	0.73–0.82	—	—	⩽0.32	—	⩽0.43	—	4	—
4	R′R″R‴P	SnX_4	0.56–0.91	0.83–1.13	1.3	⩽1.18	⩽1.13	⩽1.5	⩽1.3	32	5
	»	$SnRX_3$	1.23	—	—	1.73	—	1.41	—	1	—
5	$R'_2P(CH_2)_{1(2)}R''_{2(1)}N$	SnX_4	0.50–0.70	—	—	⩽0.50	—	⩽1	—	3	—
6	$R'_2P(O)(CH_2)_{1(2)}R''_{2(1)}N$	SnX_4	0.38–0.48	0.60–0.70	1.7	⩽0.50	⩽0.50	⩽1	⩽0.8	5	4
7	$R'_2P(S)(CH_2)_{1(2)}R''_{2(1)}N$	SnX_4	0.45–0.52	—	—	⩽0.40	—	0.8	—	3	—
8	R'_3PNR''	SnX_4	0.29–0.36	—	—	0.0	—	0.0	—	3	—
9	R′R″P(O)O⁻	SnX_2^{**}	0.09–0.15	0.16–0.22	—	⩽0.32	0.50–0.63	0–10	3.1–4.1	7	2
10	R′R″P(S)S⁻	SnX_2	0.69–0.73	0.91	—	⩽0.38	0.0	⩽0.53	0	3	1

* and ** For X = I, $\delta = 0.93$ and 0.40–0.45 mm s^{-1} respectively, $\Delta E = 0$ and 0.65–0.79 mm s^{-1}, and the number of compounds is unity.

*** For $[Cl_3P(O)]_2SnCl_4$, $\Delta E = 1.12$ mm s^{-1}.

The data in Table 1 show that there is a definite relation between δ and the electronegativity χ of the atoms surrounding the Mössbauer isotope, which makes it possible to determine the donor atom in ligands having two and more donor centres and to estimate the sequence in the variation of the isomer shift on passing from tin(IV) chloride to tin(IV) bromide complexes. This relation is described approximately by the following empirical equation[38]

$$\frac{\delta_{Br}}{\delta_{Cl}} = \alpha \frac{\chi_{Br} - \chi_{Sn}}{\chi_{Cl} - \chi_{Sn}} + \beta \frac{\chi_{Br} - \chi_{Sn}}{\chi_{Y} - \chi_{Sn}} , \qquad (2)$$

where α and β are coefficients and χ_Y is the electronegativity of the ligand donor atom.

Table 2. The Mössbauer parameters of complexes of tin(IV) chloride with phosphoryl compounds $[R'R''R'''P(O)]_2SnCl_4$ at 78–90 K.

No.	R′	R″	R‴	δ, mm s^{-1}	ΔE, mm s^{-1}	Γ_1, mm s^{-1}	Γ_2, mm s^{-1}	Refs.
1	CH_3	CH_3	CH_3	0.28	0.54	0.99	0.99	[75]
2	CH_3	CH_3	CH_3O	0.32	0.25	0.98	0.98	[74]
3	CH_3	CH_3	CH_3S	0.31	—	1.38	—	[25,32]
4	CH_3	CH_3	Cl	0.36	0.57	1.24	1.15	[74]
5	CH_3	CH_3	H	0.29	0.41	0.86	0.86	[96,97]
6	CH_3	Cl	Cl	0.87	0.50	1.66	—	[26]
7	CH_3	$(CH_3)_2N$	$(CH_3)_2N$	0.25	0.52	0.90	0.85	[31,36]
8	CH_3	C_6H_5	C_6H_5	0.31	0.68	0.92	0.89	[36,38]
9	C_6H_5	C_2H_5	C_2H_5	0.21	0.00	1.19	—	[24]
10	C_2H_5	C_2H_5	CH_3S	0.32	—	1.28	—	[25,34]
11	C_2H_5	C_2H_5	C_2H_5S	0.35	0.50	1.80	—	[25,36]
12	C_2H_5	C_2H_5	C_3H_7S	0.37	—	1.38	—	[25]
13	C_2H_5	Cl	Cl	0.46	0.78	1.05	1.05	[54]
14	C_2H_5	C_6H_5	Cl	0.34	0.46	1.22	1.22	[36,38]
15	C_2H_5	$(CH_3)_2N$	$(CH_3)_2N$	0.26	0.53	0.83	0.85	[31,36]
16	C_2H_5	C_6H_5	C_6H_5	0.36	—	0.95	—	[110]
17	C_2H_5O	C_2H_5O	$(C_6H_5)_2N$	0.38	0.64	0.96	0.94	[110]
18	n-C_3H_7	n-C_3H_7	CH_3S	0.37	—	1.28	—	[25,36]
19	iso-C_3H_7	iso-C_3H_7	CH_3S	0.32	0.83	2.02	—	[25,36]
20	n-C_4H_9	n-C_4H_9	n-C_4H_9	0.24	—	1.15	—	[21,23]
	»	»	»	0.25	0.25	0.89	0.89	[74]
21	n-C_4H_9	n-C_4H_9	H	0.36	0.39	0.84	0.86	[110]
22	CH_3O	CH_3O	CH_3O	0.37	0.53	0.95	0.95	
23	CH_3O	CH_3O	CH_3	0.37	0.53	0.95	0.95	[109]
24	CH_3O	CH_3O	$(CH_3)_2N$	0.36	0.96	0.92	0.92	[31,36]
25	CH_3O	CH_3O	C_6H_5	0.31	0.49	0.84	0.84	[96,97]
26	CH_3O	CH_3O	p-ClC_6H_4	0.26	0.53	0.89	0.89	[96,97]
27	CH_3O	CH_3O	H	0.46	0.40	0.86	0.87	[110]
28	CH_3O	CH_3O	Cl	0.35	0.68	0.86	0.83	[110]
29	CH_3O	$(CH_3)_2N$	$(CH_3)_2N$	0.36	0.35	1.04	1.04	[36]
30	C_2H_5O	C_2H_5O	CH_3S	0.37	—	1.38	—	[25,34]
31	n-C_3H_7O	n-C_3H_7O	CH_3S	0.32	0.83	2.02	—	[25,36]
32	iso-C_3H_7O	iso-C_3H_7O	CH_3S	0.37	1.06	2.27	—	[25,34,36]
33	n-C_4H_9O	n-C_4H_9O	CH_3S	0.37	0.4	1.57	—	[25,34,26]
34	C_6H_5	C_6H_5	C_6H_5	0.27	0.51	0.82	0.84	[21,23]
35	C_6H_5	C_6H_5	$(CH_3)_2N$	0.27	0.77	0.80	0.80	[36]
36	C_6H_5	C_6H_5	Cl	0.37	0.78	0.96	0.96	[36]
	»	»	»	0.42	0.78	0.92	0.92	[110]
37	C_6H_5	C_6H_5	Br	0.35	0.68	0.85	0.87	[110]
38	C_6H_5	$(CH_3)_2N$	$(CH_3)_2N$	0.28	0.61	0.86	0.85	[31,36]
39	C_6H_5	Cl	Cl	0.46	1.60	1.10	1.10	[21,23]
	»	»	»	0.46	1.45	1.10	1.10	[26,35,36]
40	C_6H_5O	C_6H_5O	C_6H_5O	0.34	0.71	0.74	0.79	[21,23]
41	C_6H_5O	C_6H_5O	Cl	0.38	0.75	0.89	0.83	[21,23]
42	C_6H_5O	Cl	Cl	0.42	1.13	0.84	0.83	[21,23]
43	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	0.31	0.70	—	—	[10,23]
	»	»	»	0.33	0.69	0.91	0.90	[31,36,74]
	»	»	»	0.23	0.75	0.79	0.79	[96,97]
44	$(CH_3)_2N$	$(CH_3)_2N$	p-$CH_3OC_6H_4$	0.27	0.70	0.83	0.83	[36]
	»	»	»	0.28	0.63	0.93	0.93	[96,97]
45	$(CH_3)_2N$	$(CH_3)_2N$	p-$CH_3OC_6H_4$	0.28	0.63	0.93	0.93	[36]
46	$(CH_3)_2N$	$(CH_3)_2N$	p-ClC_6H_4	0.30	0.72	0.89	0.89	[36]
	»	»	»	0.295	0.72	0.89	0.89	[96,97]
47	$(CH_3)_2N$	$(CH_3)_2N$	H	0.38	—	1.15	—	[110]
48	$(CH_3)_2N$	$(CH_3)_2N$	CH_2Cl	0.45	0.79	0.91	0.87	[31,36]
49	Cl	Cl	Cl	0.51	1.42	0.88	0.99	[21,23]
50	Cl	Cl	p-$CH_3OC_6H_4$	0.41	0.98	0.96	0.96	[36]
	»	»	»	0.41	0.96	0.98	0.98	[96,97]
51	Cl	Cl	p-ClC_6H_4	0.42	0.97	0.88	0.88	[36]
52	Cl	Cl	CH_2Cl	0.45	1.42	0.91	0.92	[31]
53	Cl	Cl	C_6H_4S	0.44	1.51	1.00	1.00	[109]
54	p-$(CH_3)_2NC_6H_4$	p-$(CH_3)_2NC_6H_4$	p-$(CH_3)_2NC_6H_4$	0.28	0.52	0.90	0.90	[109]
55	Cl	Cl	C_5H_5N	0.35	0.45	0.81	0.81	[109]
56	CH_3	CH_3O	H	0.35	—	1.11	—	[110]
57	C_2H_5O	C_2H_5O	Cl	0.40	0.52	0.94	0.94	[110]
58	n-C_4H_9O	n-C_4H_9O	Cl	0.34	0.72	0.90	0.90	[110]
59	C_6H_5O	C_6H_5O	$(C_6H_5)_2N$	0.37	—	1.10	—	[110]
60	C_6H_5	C_6H_5	$(C_6H_5)_2P$	0.30	0.49	1.13	1.13	[110]

Note. For complexes 5, 25, 26, 43, 44, 46, and 50, the values of f'_{85} are respectively 0.31, 0.31, 0.15, 0.36, 0.23, 0.26, and 0.29.[96,97]

The data in Table 1 and Eqn.(2) suggest[38] that the complexes $[(C_5H_{10}N)P(S)]_2SnCl_4$ and $[(C_4H_8N)P(S)]_2SnCl_4$, whose isomer shifts are 0.49 and 0.43 mm s^{-1} respectively, are formed as a consequence of the electron-donating properties of the nitrogen atom and not the thiophosphoryl sulphur, as suggested by Carty and Sharma[23]. The above conclusion is confirmed by data obtained for similar systems in ^{35}Cl Mössbauer spectroscopic and vibrational spectroscopic studies[44].

Table 3. The Mössbauer parameters of complexes of tin(IV) bromide with phosphoryl compounds $[R'R''R'''P(O)]_2SnBr_4$ at 78–90 K.

No.	R′	R″	R‴	δ, mm s^{-1}	ΔE, mm s^{-1}	Γ_1, mm s^{-1}	Γ_2, mm s^{-1}	References
1	CH_3	CH_3	CH_3O	0.65	0.4	1.51	—	[26,27]
2	CH_3	CH_3	CH_3S	0.60	—	1.42	—	[25,26,34]
3	CH_3	CH_3	H	0.61	—	1.20	—	[110]
4	CH_3	CH_3	Cl	0.66	—	1.20	—	[26]
5	CH_3	C_6H_5	C_6H_5	0.62	0.37	0.83	0.83	[38]
6	CH_3	$(CH_3)_2N$	$(CH_3)_2N$	0.64	—	1.03	—	[31]
7	C_2H_5	C_2H_5	CH_3S	0.63	—	1.11	—	[25]
8	C_2H_5	$(CH_3)_2N$	$(CH_3)_2N$	0.64	0.36	1.07	1.07	[31]
9	CH_3O	CH_3O	C_6H_5	0.61	1.04	0.92	0.92	
10	C_2H_5O	C_2H_5O	$CH_2CH_2C_6H_4N$	0.76	0.50	1.03	1.03	[36,97,109]
11	C_6H_5	C_6H_5	$(CH_3)_2N$	0.54	0.71	0.80	0.80	[31]
12	C_6H_5	C_6H_5	Br	0.67	0.61	0.79	0.79	[110]
13	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	0.56	0.76	—	—	[23]
	»	»	»	0.57	0.805	0.92	0.92	[96,97]
14	p-$(CH_3)_2NC_6H_4$	p-$(CH_3)_2NC_6H_4$	p-$(CH_3)_2NC_6H_4$	0.56	0.52	0.91	0.91	[109]
15	C_2H_5	C_2H_5	C_2H_5	0.79	—	1.24	—	[24]
16	n-C_4H_9	n-C_4H_9	n-C_4H_9	0.91	—	1.61	—	[24]
17	C_6H_5	C_6H_5	$(C_6H_5)_2N$	0.60	1.11	0.85	0.82	[110]
18	n-C_3H_7	C_6H_5	C_6H_5	0.64	0.05	1.45	—	[110]
19	C_6H_5	C_6H_5	Cl	0.67	—	0.86	—	[110]

Note. $f'_{85K} = 0.40$ for complex 13.[96,97]

Table 4. The Mössbauer parameters of complexes of alkyltin halides with phosphoryl compounds $[R'R''R'''P(O)]_2SnR_n \cdot Cl_{4-n}$ at 78–90 K.

No.	R′	R″	R‴	R	n	δ, mm s^{-1}	ΔE, mm s^{-1}	Γ_1, mm s^{-1}	Γ_2, mm s^{-1}	References
1	CH_3	CH_3	CH_3	CH_3	2	1.38	4.30	1.12	1.18	[26,28,74]
2	CH_3	CH_3	CH_3O	CH_3	1	0.90	2.20	1.20	1.25	[26,28,74]
3	CH_3	CH_3	CH_3O	CH_3	2	1.50	4.37	1.27	1.27	[26,28,74]
4	CH_3	CH_3	CH_3S	CH_3	2	1.45	4.20	1.20	1.20	[26]
5	CH_3	CH_3	Cl	CH_3	1	1.04	2.26	1.15	1.24	[26,28,74]
6	CH_3	CH_3	Cl	CH_3	2	1.58	4.10	1.06	1.28	[26,28,74]
7	CH_3	CH_3	Cl	C_2H_5	1	1.47	2.25	1.11	1.10	[26,28]
8	CH_3	CH_3	Cl	n-C_4H_9	1	1.06	2.30	1.23	1.32	[26,28]
9	C_2H_5	C_2H_5	CH_3S	CH_3	2	1.45	4.15	1.35	1.36	[26]
10	C_2H_5	C_2H_5	CH_3S	C_2H_5	1	1.10	2.10	1.25	1.25	[26]
11	n-C_3H_7	n-C_3H_7	CH_3S	CH_3	2	1.43	4.20	1.25	1.35	[26]
12	iso-C_3H_7	iso-C_3H_7	CH_3S	CH_3	2	1.56	4.05	1.19	1.19	[26]
13	n-C_4H_9	n-C_4H_9	n-C_4H_9	CH_3	2	1.34	4.22	0.82	0.82	[74]
14	n-C_4H_9	n-C_4H_9	n-C_4H_9	n-C_4H_9	2	1.49	4.13	0.85	0.93	[20]
15	n-C_4H_9	n-C_4H_9	n-C_4H_9	C_6H_5	2	1.20	3.81	0.95	1.01	[20]
16	C_2H_5O	C_2H_5O	CH_3S	CH_3	2	1.47	4.00	1.10	1.25	[26]
17	C_6H_5	C_6H_5	C_6H_5	n-C_4H_9	1	1.05	2.36	0.97	0.96	[20]
	»	»	»	»	1	1.10	2.32	—	—	[105,106]
18	C_6H_5	C_6H_5	C_6H_5	CH_3	2	1.37	4.30	1.15	1.02	[88]
19	C_6H_5	C_6H_5	C_6H_5	n-C_4H_9	2	1.62	4.11	0.97	1.03	[20]
20	C_6H_5	C_6H_5	C_6H_5	C_6H_5	1	0.80	2.01	1.19	1.38	[20]
21	C_6H_5	C_6H_5	C_6H_5	C_6H_5	2	1.25	3.98	0.97	1.00	[20]
22	C_6H_5	C_6H_5	$(CH_3)_2N$	CH_3	1	0.63	1.99	0.96	0.86	[96,97]
23	C_6H_5	C_6H_5	$(CH_3)_2N$	CH_3	2	1.26	3.95	0.80	0.80	
24	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	CH_3	1	0.89	2.35	—	—	[21]
25	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	CH_3	2	1.50	4.36	—	—	[21]
	»	»	»	»	»	1.32	4.28	1.27	1.06	[88]
	»	»	»	»	»	1.38	4.09	0.94	0.94	[96,97]

Note. The values of f'_{85K} have been determined for complexes 22 and 25 (0.29 and 0.38).[96,97]

In selecting the coefficients α and β in Eqn.(2), it was found that the optimum agreement between the calculated and experimental δ_{Br}/δ_{Cl} (Table 1) is observed when the ligands are subdivided into groups with similar electronegativities:

(a) the Allred–Rochow electronegativities[45,46]:

Y=O, N, Cl : α=2.61, β=—0.88;
Y=S, P, Br : α=1.69, β=—0.085;

(b) the Pauling electronegativities[45,47,48]:

Y=O, N, Cl : α=2.94, β=—0.85;
Y=S, P, Br : α=2.82, β=—0.055;

(c) the Mulliken electronegativities[23,49–51]:

Y=O, N, Cl : α=4.90, β=—2.89;
Y=S, P, Br : α=2.55, β=—0.48.

Table 5. The Mössbauer parameters of complexes of trialkyl-(aryl)tin chlorides $[R'R''R'''P(O)]SnR_3Cl$ at 78–90 K.

R′	R″	R‴	R	δ, mm s^{-1}	ΔE, mm s^{-1}	Γ_1, mm s^{-1}	Γ_2, mm s^{-1}	References
CH_3	CH_3	CH_3O	CH_3	1.38	3.65	1.20	1.10	[26,28]
CH_3	CH_3	Cl	CH_3	1.52	3.50	1.25	1.28	[26,28]
CH_3O	CH_3O	CH_3O	C_6H_5	1.31	3.18	—	—	[107]
C_6H_5	C_6H_5	C_6H_5	C_6H_5	1.29	3.14	—	—	[107]
C_6H_5O	C_6H_5O	C_6H_5O	C_6H_5	1.31	3.07	—	—	[107]
C_6H_5O	C_6H_5O	C_6H_5O	C_6H_5	1.30	3.15	—	—	[107]
C_6H_5	C_6H_5	C_6H_5	CH_3	1.45	3.49	—	—	[105,106]
$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	CH_3	1.44	3.52	—	—	[105,106]
$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	C_6H_5	1.43	3.47	0.77	0.77	[26]

Table 6. The Mössbauer parameters of complexes of tin tetrahalides with organophosphorus compounds containing tervalent phosphorus $[R'R''R'''P]_2SnX_4$ at 78–90 K.

No.	R′	R″	R‴	δ, mm s^{-1}	ΔE, mm s^{-1}	Γ_1, mm s^{-1}	Γ_2, mm s^{-1}	References
1	C_2H_5	C_2H_5	C_2H_5	0.87	0.95	0.52	0.54	[20,23]
2	C_2H_5	C_2H_5	$n\text{-}C_3H_7S$	0.82	0.91	0.97	0.97	[32]
	»	»	»	0.81	0.96	1.09	1.09	[96,97]
3	C_2H_5	C_2H_5	C_6H_5	0.88	0.99	0.74	0.71	[19]
4	C_2H_5	C_2H_5	Cl	0.75	0.49	0.89	0.89	[32]
	»	»	»	0.71	0.60	1.03	1.03	[96,97]
5	C_2H_5	C_2H_5	C_2H_5S	0.80	0.50	1.70	—	[26]
6	C_2H_5	$n\text{-}C_3H_7$	$n\text{-}C_3H_7S$	0.62	0.53	0.84	0.84	[32]
	»	»	»	0.63	0.57	0.91	0.91	[96,97]
7	C_2H_5	$(CH_3)_2N$	$(CH_3)_2N$	0.85	1.10	1.25	0.86	[31]
	»	»	»	0.85	1.02	1.03	1.03	[32]
8	C_2H_5	$n\text{-}C_3H_7$	Cl	0.70	0.57	0.97	0.97	[32]
9	C_2H_5	C_6H_5	Cl	0.57	0.46	0.84	0.84	
10	C_2H_5	C_6H_5	C_6H_5	0.63	0.46	0.83	0.86	[19]
11	C_2H_5O	C_2H_5O	$(C_2H_5)_2N$	0.64	0.4	1.30	—	[110]
12	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	0.89	0.95	0.78	0.73	[19,23]
13	$iso\text{-}C_3H_7$	$iso\text{-}C_3H_7$	CH_3S	0.83	0.38	0.92	0.92	[32]
	»	»	»	0.83	0.37	1.04	1.04	[96,97]
14	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	0.85	1.02	0.78	0.76	[19,23]
	»	»	»	0.85	1.17	1.28	1.06	[24]
	»	»	»	0.86	1.02	1.17	1.28	[31,34]
	»	»	»	0.87	1.07	0.97	0.97	[97]
15	CH_3O	CH_3O	CH_3O	0.63	0.54	1.01	1.01	[32,35]
16	$n\text{-}C_3H_7S$	$n\text{-}C_3H_7S$	$n\text{-}C_3H_7S$	0.66	0.52	0.86	0.86	[32]
	»	»	»	0.68	0.51	1.00	1.00	[96,97]
17	C_6H_5	C_6H_5	C_6H_5	0.75	—	0.81	—	[19,23]
	»	»	»	0.66	0.31	0.87	0.87	[97]
18	C_6H_5	C_6H_5	C_6H_5	0.95	—	—		[23]
	»	»	»	0.85		0.95		
19	C_6H_5	C_6H_5	CH_3	0.81	0.58	0.66	0.64	[19,23]
20	C_6H_5	C_6H_5	CH_3O	0.81	0.45	0.72	0.68	[19,23]
21	C_6H_5	C_6H_5	$C{\equiv}CCH_3$	0.77	—	0.89	—	[19,23]
22	C_6H_5	C_6H_5	$(CH_3)_2N$	0.83	0.50	1.07	1.07	[32,108]
23	C_6H_5	C_6H_5	Cl	0.70	—	1.45	—	[26]
24	C_6H_5	C_6H_5	Cl	0.86	—	0.96	—	[38]
25	C_6H_5	C_6H_5	Br	0.89		0.92	—	[38]
26	C_6H_5	C_6H_5	$CH_2CH_2C_6H_4N$	0.69	—	0.97	—	[109]
27	C_6H_5	CH_3	CH_3	0.85	0.97	0.68	0.68	[10,23]
	»	»	»	0.91	1.18	1.24	1.12	[24]
28	C_6H_5	$(CH_3)_2N$	$(CH_3)_2N$	0.80	1.20	1.10	1.15	[31,36]
29	C_6H_5	C_6H_5	$(C_6H_5)_2N$	0.85	—	1.10	—	
30	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	0.74	0.59	0.90	0.90	[97]
	»	»	»	0.74	0.58	0.97	0.97	[32,38]
31	$(CH_3)_2N$	$(CH_3)_2N$	$p\text{-}CH_3OC_6H_4$	0.79	0.75	0.96	0.96	[34]
	»	»	»	0.79	0.70	0.96	0.96	[32]
32	$(CH_3)_2N$	$(CH_3)_2N$	$p\text{-}ClC_6H_4$	0.77	0.69	0.94	0.94	[32]
	»	»	»	0.77	0.72	0.94	0.89	[36]
33	$(CH_3)_2N$	Cl	Cl	0.56	0.4	1.45	—	[108]
34	CH_3	CH_3	C_2H_5	1.13	1.13	1.41	1.07	[24]
35	C_8H_{17}	C_8H_{17}	C_8H_{17}	0.72	1.08	0.94	1.17	[24]
36	C_8H_{17}	C_8H_{17}	C_8H_{17}	0.94	0.89	—	—	[24]

Note. X = Br in complexes 18, 24, 25, 34, and 35, while in the remaining cases X = Cl. f'_{85K} = 0.41, 0.31, 0.22, 0.21, 0.25, 0.25, 0.31, and 0.29 for complexes 2,4,6,13,14,16,17, and 30 respectively[96,97].

We may note that the correlations between the isomer shifts and the Mulliken group molecular electronegativities of the ligands (χ_L) in similar complexes has also been mentioned by Carty and Sharma[23]. The use of χ_L from their study[23] in Eqn.(2) instead of χ_Y also leads to satisfactory results.

Table 7. The Mössbauer parameters of complexes of tin tetrahalides with thio- and seleno-phosphoryl compounds $[R'R''R'''P(Y)]_2SnX_4$ at 78–90 K.

No.	R′	R″	R‴	X	δ, mm s^{-1}	ΔE, mm s^{-1}	Γ_1, mm s^{-1}	Γ_2, mm s^{-1}	References
1	CH_3	CH_3	CH_3O	Cl	0.65	—	1.10	—	[26,28,36]
2	CH_3	CH_3	CH_3O	Br	1.07	—	1.38	—	[26,28]
3	CH_3	CH_3	$(CH_3)_2N$	Cl	0.66	0.32	1.00	1.00	[36]
4	CH_3	CH_3	Cl	Cl	0.64	—	1.20	—	[26,28,36]
5	CH_3	$(CH_3)_2N$	$(CH_3)_2N$	Cl	0.67	—	0.92	—	[31]
6	CH_3	$(CH_3)_2N$	$(CH_3)_2N$	Br	0.86	0.31	0.99	0.99	[31]
7	CH_3	$(CH_3)_2N$	Cl	Cl	0.66	0.42	0.97	0.97	[31]
8	C_2H_5	C_2H_5	C_2H_5S	Cl	0.69	—	1.05	—	[26,36]
9	C_2H_5	C_2H_5	CH_3S	Cl	0.71	—	1.25	—	[25,26]
10	C_2H_5	C_2H_5	CH_3S	Br	0.88	—	1.27	—	[25,26]
11	C_2H_5	C_2H_5	$n\text{-}C_3H_7S$	Cl	0.60	—	1.20	—	[26]
12	C_2H_5	C_2H_5	$(CH_3)_2N$	Cl	0.66	—	1.10	—	[108]
13	C_2H_5	C_2H_5	$(CH_3)_2N$	Br	0.96	—	0.89	—	[108]
14	C_2H_5	C_2H_5	Cl	Cl	0.65	0.50	1.20	1.20	[35]
15	C_2H_5	$(CH_3)_2N$	$(CH_3)_2N$	Cl	0.66	0.32	0.91	0.91	[31,36]
16	C_2H_5	$(CH_3)_2N$	$(CH_3)_2N$	Br	0.94	—	1.15	—	[31]
17	C_2H_5	$(CH_3)_2N$	Cl	Cl	0.67	—	1.20	—	[36]
18	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	CH_3S	Cl	0.60	—	1.25	—	[25,26]
19	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	CH_3S	Br	0.99	0.4	1.56	—	[25,26]
20	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	Cl	0.64	—	1.10	—	[31]
21	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	CH_3S	Br	0.88	—	1.36	—	[25,26]
22	C_6H_5	C_6H_5	$(CH_3)_2N$	Cl	0.60	0.3	1.28	—	[108]
23	C_6H_5	C_6H_5	$(CH_3)_2N$	Br	0.95	0.3	1.35	—	[108]
24	C_6H_5	C_6H_5	$CH_2CH_2C_6H_4N$	Cl	0.53	0.32	0.92	—	[109]
	»	»	»	Cl	0.53	—	1.00	—	[109]
25	C_6H_5	$(CH_3)_2N$	$(CH_3)_2N$	Cl	0.70	0.35	0.90	0.90	[31,36]
26	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	Cl	0.65	—	0.83	—	[31]
27	$(CH_3)_2N$	$(CH_3)_2N$	$p\text{-}ClC_6H_4$	Cl	0.62	0.39	1.08	1.01	[36]
	»	»	»	Cl	0.62	0.59	1.01	1.01	
28	C_2H_5	$(CH_3)_2N$	$(CH_3)_2N$	Cl	0.82	0.27	1.07	1.06	[31]
29	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	Cl	0.74	0.32	0.93	0.93	[31]
30	C_6H_5	C_6H_5	$(CH_3)_2N$	Cl	0.75	—	0.93	—	[31]
31	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	Cl	0.73	—	1.18	—	[31]

Note. Y = Se for compounds 28–31, while in the remaining cases Y = S.

Table 8. The Mossbauer parameters of the salts $[R_2P(Y)Y]_2.SnX_2$ at 78–90 K.

No.	R	Y	X	δ, mm s^{-1}	ΔE, mm s^{-1}	Γ_1, mm s^{-1}	Γ_2, mm s^{-1}	f'_{85} K	References
1	CH_3	O	Cl	0.07	—	1.20	—	—	[26]
2	$\frac{1}{2}(CH_3)(CH_3O)$	O	Cl	0.02	—	1.43	—	—	[26]
3	C_2H_5	S	Cl	0.73	—	1.18	—	—	[26]
	»	S	Cl	0.76	—	0.92	—	0.37	[96,97]
4	$n\text{-}C_3H_7$	S	Cl	0.71	—	1.46	—	—	[26]
	»	S	Cl	0.72	0.38	1.03	1.03	0.36	[96,97]
5	$n\text{-}C_4H_9$	O	Cl	0.00	—	1.45	—	—	[26]
	»	O	Cl	0.03	0.32	0.92	0.92	0.57	[96,97]
6	CH_3O	O	Cl	0.04	—	1.42	—	—	[26]
7	C_6H_5	O	Cl	0.05	—	1.43	—	—	[26]
8	C_6H_{11}	O	Cl	0.66	—	1.27	—	—	[26]
9	C_6H_5	O	Br	0.16	0.5	1.70	—	—	[26]
	»	O	Br	0.18	0.63	0.81	0.81	0.52	[96,97]
10	C_2H_5O	O	Br	0.13	0.53	0.86	0.87	—	[54]
11	C_2H_5O	O	Cl	0.02	—	1.33	—	—	[54]
12	$iso\text{-}C_3H_7O$	S	Cl	0.72	0.21	0.85	0.85	—	[110]
13	$iso\text{-}C_3H_7O$	S	Br	0.91	—	0.95	—	—	[110]
14	C_6H_5	O	I	0.40	0.65	0.87	0.87	—	[110]

Together with the Mössbauer spectra of the molecular complexes of tin halides with organophosphorus compounds, Mananov et al.[26] investigated the Mössbauer spectra of the salt products $[R'R''P(Y)Y]_2SnX_2$ (Table 8). The similarity

of the values of δ for the complexes $[R'R''P(O)O_2]SnCl_2$ to those for SnO_2 and $BaSnO_3$ suggests that the immediate environment of the tin atom in these complexes is also octahedral[52,53]. This is possible for the polymeric structure $[R'R''P(O)O]_2SnCl_2$, which is in full agreement with data obtained for the above and similar compounds by vibrational spectroscopic methods[54].

2. The Effects of Substituents

Together with the influence of the immediate environment of the tin atom in the complexes $[R'R''R'''P(Y)]_{2(1)}SnR_nX_{4-n}$, on the isomer shift, the study of the influence of the substituents in $R'R''R'''P(Y)$ and SnR_nX_{4-n} on the isomer shifts of the complexes $L_2SnR_nX_{4-n}$ and the estimation of the degree of their influence on the population of the 5*s* shell of the tin atom are also of undoubted interest. The tendency towards a linear dependence of δ on the sum of the constants of the substituents in the ligand and the acceptor was noted in our earlier studies[26,31,32,40-42,54] and by Khrapov et al.[55] and Ford and Sams[56].

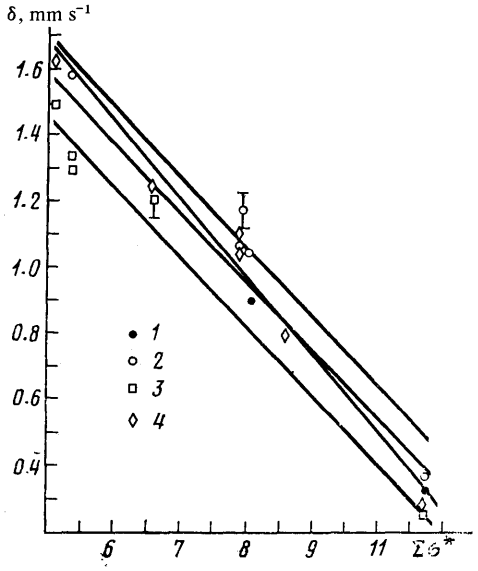


Figure 2. Relations between δ and $\Sigma\sigma^*_{R,Cl}$ for different complexes: 1) $[(CH_3)_2(CH_3O)P(O)]_2Sn(CH_3)_nCl_{4-n}$; 2) $[(CH_3)_2ClP(O)]_2SnR_nCl_{4-n}$ (R = CH_3, C_2H_5, or C_4H_9; 3) $[(n\text{-}C_4H_9)_3P(O)]_2SnR_nCl_{4-n}$ (R = CH_3, C_2H_5, or C_6H_5); 4) $[(C_6H_5)_3P(O)]_2SnR_nCl_{4-n}$ (R = C_4H_9 or C_6H_5).

Analysis of the dependence of δ on the sum of the Taft constants[57,58] of the substituents at the tin atom (Σσ*) leads to the following correlation equations† (Fig. 2):

$$[(CH_3)_2(CH_3O)P(O)]_2Sn(CH_3)_nX_{4-n}\ (n = 0, 1, 2;\ X = Cl, Br) \quad (3a)$$
$$\delta = -0.206\,\Sigma\sigma^* + 2.600\ (r = 0.984,\ S = 0.076,\ P \leqslant 0.0027,\ m = 4),$$

$$[(CH_3)_2ClP(O)]_2SnR_nX_{4-n}\ (n = 0, 1, 2;\ X = Cl, Br;\ R = CH_3, C_2H_5, C_4H_9) \quad (3b)$$
$$\delta = -0.213\,\Sigma\sigma^* + 2.770\ (r = 0.984,\ S = 0.0067,\ P < 0.0005,\ m = 7),$$

$$[(n\text{-}C_4H_9)_3P(O)]_2SnR_nCl_{4-n}\ (n = 0, 1, 2;\ R = CH_3, C_4H_9, C_6H_5) \quad (3c)$$
$$\delta = -0.210\,\Sigma\sigma^* + 2.501\ (r = 0.994,\ S = 0.057,\ P \leqslant 0.0008,\ m = 6),$$

$$[(C_6H_5)_3P(O)]_2SnR_nX_{4-n}\ (n = 0, 1, 2;\ X = Cl, Br;\ R = CH_3, C_4H_9, C_6H_5) \quad (3d)$$
$$\delta = -0.206\,\Sigma\sigma^* + 2.606\ (r = 0.972,\ S = 0.094,\ P < 0.0005,\ m = 8).$$

Evidently the coefficients representing the slopes in Eqns. (3a)–(3d) change insignificantly from series to series. This suggests that the Sn–Cl, Sn–Br, and Sn–C bonds make the main contribution to the population of the 5*s* valence shell of the tin atom in the complexes $[R'R''R'''P(O)]_{2(1)}\cdot SnR_nX_{4-n}$. This conclusion is consistent with those reached from the dependence of δ on χ[23,51] and with X-ray diffraction data[60].

The dependence of δ on Σσ* for the substituents at the tin atom and on the sum of the Kabachnik constants ($\Sigma\sigma^{ph}$)[57,58] for the substituents at the phosphorus atom were examined by ourselves[40] to estimate the influence of the substituents at both tin and phosphorus atoms on the isomer shift in the Mössbauer spectra of the complexes $[R'R''R'''P(O)]_2SnR_nX_{4-n}$#:

$$\delta = -0.208\Sigma\sigma^* + 0.018\Sigma\sigma^{ph} + 2.635\ (r = 0.976,\ S = 0.095,\ P < 0.0005,\ m = 90). \quad (4)$$

Comparison of Eqns. (3) and (4) shows that allowance for the influence on δ by the nature of the substituents at the phosphorus atom together with that of the substituents at the tin atom does not introduce significant changes into the constant term and the coefficient of Σσ*.

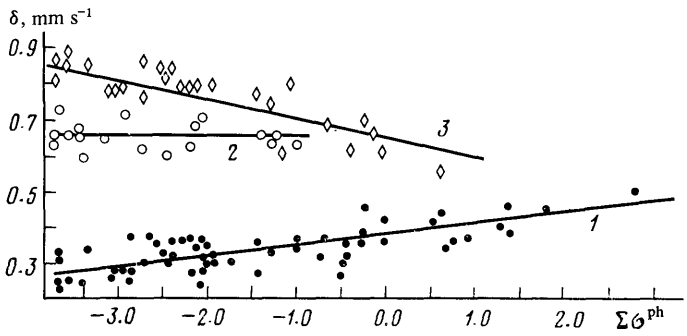


Figure 3. Relations between δ and $\Sigma\sigma^{ph}$ for the complexes $[R'R''R'''P(Y)]_2SnCl$: 1) Y = O; 2) Y = S; 3) Y = LEP.

Examination of the Mössbauer parameters of the complexes $[R'R''R'''P(Y)]_2SnCl_4$ shows that here too there is a tendency towards a linear variation of δ as a function of the sum of the constants of the substituents at the phosphorus atom[32,37,40,54] (Fig. 3):

$$[R'R''R'''P(O)]_2SnCl_4 \quad (5a)$$
$$\delta = 0.030\,\Sigma\sigma^{ph} + 0.381\ (r = 0.78,\ S = 0.039,\ P < 0.0005,\ m = 48),$$

† The two-parameter linear correlation equations have been obtained by the method of least squares[59]. Here and below the following notation has been adopted: *r* is the correlation coefficient, *S* the main error, *P* the level of significance, and *m* the number of experimental points.

Numerous correlation equations have been obtained by the Chebyshev method[61].

$$[R'R''R'''P(S)]_2SnCl_4 \quad (5b)$$
$$\delta = 0.66 \pm 0.06,$$
$$[R'R''R'''P]_2SnCl_4 \quad (5c)$$
$$\delta = 0.056\,\Sigma\sigma^{ph} + 0.646\,(r = 0.75, S = 0.061, P < 0.0005, m = 28),$$
$$[R'R''R'''P]_2SnR_nX_{4-n}\ (X=Cl,\ Br;\ n=0.1;\ R=C_4H_9) \quad (5d)$$
$$\delta = -0.196\,\Sigma\sigma^* - 0.055\,\Sigma\sigma^{ph} + 2.768\,(r = 0.84,$$
$$S = 0.075,\ P < 0.0005,\ m = 32).$$

It is seen from Eqns.(5) that, as the nature of the donor centre varies from Y = O to Y = LEP (lone electron pair), the sign of the slope changes. In the reaction series investigated the sensitivity to the nature of the substituents at the phosphorus atom in the ligand decreases in the sequence $R'R''R'''P > R'R''R'''P(O) > R'R''R'''P(S)$. On the other hand, the sensitivity of the enthalpy of complex formation ΔH to the influence of the substituents decreases in the sequence $> R'R''R'''P(S) > R'R''R'''P > R'R''R'''P(O)$.[62,63] The observed difference can be due to small (in absolute magnitude) changes in ΔH in the series of complexes of thiophosphoryl compounds investigated by Mössbauer spectroscopy ($\Delta\Delta H \leq 5$ kcal mol^{-1}).[62,63]

Since the enthalpies of formation of the complexes increase as the "electron withdrawing" effect of the substituents at the phosphorus atom is reduced for all the $[R'R''R'''P(Y)]_2 \cdot SnX_4$ (Y = O, S, Se, or LEP) investigated[62,63], one of the possible causes of the difference between the values of ρ in Eqns.(4) and (5a) and in Eqns.(5c) and (5d) can apparently be an additional donor–acceptor interaction in $[R'R''R'''P]_2 \cdot SnX_4$ between the lone electron pair of the halogen atom in the acceptor molecule and the vacant d orbitals of the phosphorus atom of the ligand molecule[32,40,63]. With increase of the basicity of the phosphorus atom in $R'R''R'''P$, the strength of this interaction should increase, since the electron density transferred from the donor is concentrated at the halogen atoms[64,65], which leads to an increase of δ.

It is known[1,4,20,23,26,61] that tin halides are capable of forming trigonal-bipyramidal complexes as well as octahedral complexes. We therefore investigated[26,40] the influence of the substituents at the tin atom and of the organophosphorus ligand on δ in pentacoordinate complexes of tin halides. A correlation analysis of the isomer shifts in the Mössbauer spectra of the complexes $LSnR_3Cl$ (Table 5) as a function of the reaction constants of the substituents at the phosphorus and tin atoms was carried out for this purpose. The resulting correlation equations are

$$\delta = -0.076\,\Sigma\sigma^* + 1.648\,(r = 0.892, S = 0.036, P \leq 0.002, m = 8), \quad (6)$$
$$\delta = -0.093\,\Sigma\sigma^* + 0.020\,\Sigma\sigma^{ph} + 1.740\,(r = 0.919, S = 0.031, P < 0.0005,$$
$$m = 8). \quad (7)$$

It is seen from Eqns.(4), (5a), (6), and (7) that in the pentacoordinate compounds the sensitivity of the isomer shift to the nature of the substituents at the tin atom is much smaller than in the octahedral complexes, while the contribution of the organophosphorus ligand to δ remains virtually the same. We believe that the above finding is due to the fact that in the octahedral systems there is a relatively symmetrical distribution of ligands about the nucleus. On the other hand, in trigonal-bipyramidal complexes this symmetry breaks down in the axial plane (L–Sn–Cl), which apparently increases the sensitivity of δ to L.[40,60,67]

Thus the isomer shifts of the compounds $[R'R''R'''P(Y)]_{2(1)} \cdot SnR_nX_{4-n}$ are described satisfactorily in terms of the reaction constants of the substituents at the tin and phosphorus atoms. The correlation equations obtained can be used to predict the isomer shifts in the Mössbauer spectra of similar compounds and their other spectroscopic characteristics[23–44], to estimate the Taft and Kabachnik constants of the substituents in the ligand and acceptor, to determine the 5s valence shell populations of the tin atom in the complexes of tetra-alkyltin compounds and alkyltin halides with organophosphorus ligands, and to determine the coordination number of tin in the compounds investigated. Since the enthalpies of formation of the complexes $[R'R''R'''P(Y)]_{2(1)}SnR_nCl_{4-n}$, characterising the energies of the donor-acceptor interaction, are likewise linearly related to $\Sigma\sigma^*$ and $\Sigma\sigma^{ph}$,[62,63] Mössbauer spectroscopy can be used also to estimate the enthalpies of formation of the complexes of tetra-alkyltin compounds and alkyltin halides with $R'R''R'''P(Y)$.

Table 9. The Mössbauer parameters of complexes of tin tetrahalides with bidentate organophosphorus compounds $LSnX_4$ at 78–90 K.

No.	L	δ, mm s^{-1}	ΔE_Q, mm s^{-1}	Γ_1, mm s^{-1}	Γ_2, mm s^{-1}	References
1	2,3-bis(diethylphosphono)butadiene	0.29	0.44	0.82	0.82	[96,97]
2	2,3-bis(diethylphosphono)butadiene	0.63	0.52	0.80	0.80	[96,97]
3	2,3-bis(diphenylphosphono)butadiene	0.35	0.66	—	—	[27]
4	2,3-bis(diphenylphosphono)butadiene	0.66	0.67	—	—	[27]
5	$(CH_3)_2P(S)P(CH_3)_2$	0.67	—	1.04	—	[28]
6	$(CH_3)_2P(S)(S)P(CH_3)_2$	0.70	—	1.13	—	[28]
7	*meso*-$CH_3C_2H_3P(S)(S)PCH_3C_2H_3$	0.70	—	1.10	—	[28]
8	racemate–$CH_3C_2H_3P(S)(S)PC_2H_3CH_3$	0.65	—	1.20	—	[28]
9	racemate–$CH_3C_2H_3P(S)(S)PC_2H_3CH_3$	0.67	—	0.99	—	[96,97]
10	$(CH_3O)_2P(O)(C_6H_5)_2$	0.42	—	1.30	—	[28]
11	$(C_6H_5)_2P(O)CH_2(C_6H_5)_2N$	0.38	0.45	0.83	0.83	[109]
12	$(C_6H_5)_2P(O)CH_2(C_6H_5)_2N$	0.60	0.45	0.99	0.99	[109]
13	$(C_6H_5)_2P(S)CH_2(C_6H_5)_2N$	0.52	0.44	0.84	0.84	[109]
14	$(C_6H_5)_2P(CH_2)(C_6H_5)_2N$	0.48	0.46	0.88	0.88	[109]
15	(α-pyridyl)P(O)Cl	0.35	—	1.00	—	[109]
16	$(C_6H_5)_2P(S)CH_2CH_2C_5H_4N$	0.45	—	1.00	—	[109]
17	$(C_6H_5)_2PCH_2CH_2C_5H_4N$	0.69	—	0.97	—	[109]
18	$(C_6H_5O)_2P(O)CH_2CH_2C_5H_4N$	0.43	—	1.08	—	[109]
		0.42	0.40	0.96	0.96	[96,97]
19	$(C_6H_5O)_2P(O)CH_2CH_2C_5H_4N$	0.70	0.46	0.96	0.96	[109]
20	$(C_6H_5)_2P(O)(O)P(C_6H_5)_2$	0.39	0.41	0.88	0.88	[110]
21	$(CH_3)_2P(O)(O)P(CH_3)_2$	0.28	0.41	0.88	0.88	[110]
22	$(C_6H_5)_2P(O)(O)P(C_6H_5)_2$	0.73	0.51	0.85	0.85	[110]
23	$(C_6H_5O)_2P(O)(O)P(C_6H_5O)_2$	0.37	0.60	0.94	0.94	[110]
24	$(CH_3)(C_6H_5)P(S)(S)P(C_6H_5)(CH_3)$	0.67	—	0.99	—	[96,97]

Note. X = Br in complexes 2,4,12,19, and 22, while in the remaining cases X = Cl. $f'_{85K} = 0.23$, 0.24, 0.22, 0.23, 0.21, and 0.22 for complexes 1,2,9,18, and 24 respectively.

III. THE QUADRUPOLE SPLITTING

1. The Influence of the Geometrical Structure of the Complexes

The electrical quadrupole interaction in the Mössbauer spectra is manifested by a fine structure whose components correspond to the gamma transitions between the split levels. For the ^{57}Fe and ^{119}Sn Mössbauer nuclei, where the spins of the excited and ground states are 3/2 and 1/2 respectively, this hyperfine structure appears in the spectrum in the form of a doublet. The appearance of the doublet is associated with the splitting of only the upper level into two states with spin projections $m_I = \pm 3/2$ and $m_I = \pm 1/2$, while the ground state with a spin of 1/2 is not split[1,4]. A typical Mössbauer spectrum with quadrupole splitting is presented in Fig.4.

The energy gap between the split sublevels (or the quadrupole splitting ΔE) can be represented as follows for ^{57}Fe and ^{119}Sn[1,4]:

$$\Delta E = -\frac{1}{2}e^2qQ\left(1 + \frac{1}{3}\eta^2\right)^{1/2}, \quad (8)$$

where Q is the quadrupole moment of the nucleus, characterising the deviation of the distribution of the averaged nuclear charge density in the state with $I = 3/2$ (for ^{57}Fe and ^{119}Sn) from spherical symmetry, $q = V_{zz}/e$ the electric field gradient (EFG) at the Mössbauer nucleus, $\eta = (V_{xx} - V_{yy})/V_{zz}$ the asymmetry parameter, and V_{xx}, V_{yy}, and V_{zz} are the principal components of the diagonalised EFG tensor chosen so that the condition $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$, for which the values of η are in the range $0 \leq \eta \leq 1$, holds.

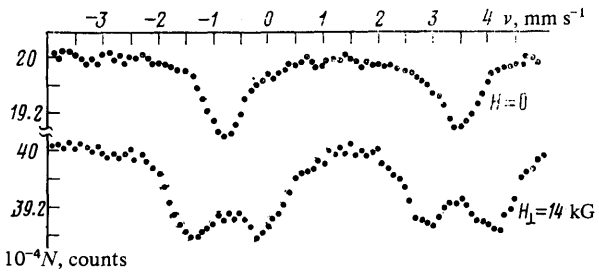


Figure 4. The Mössbauer spectra of $\{[(CH_3)_2N]_3P(O)\}_2 . Sn(CH_3)_2Cl_2$ for $H = 0$ and $H = 14$ kG.

The valence shell of the free tin atom has the structure $5s^25p^2$, but, since s electrons have the spherical symmetry (without taking shielding into account), they do not give rise to an electric field gradient at the nucleus and the EFG for ^{119}Sn depends on the distribution of p electrons. For different types of hybridisation, s and d electrons can contribute to the EFG,[1,4] but the nature of the p bond is decisive; consequently ΔE makes it possible to estimate the electron distribution in the valence p shell.

Like the isomer shift, the quadrupole splitting is a characteristic parameter for the determination of the valence state of the tin atom. In those cases where tin is in the bivalent state the absorption spectra have a doublet structure[1,4,17,68,69] ($\Delta E = 0.5-2.5$ mm s^{-1}) [with the exception of $SnCl_2$,[1,48] owing to the presence of unbalanced p electrons in tin(II) compounds giving rise to an EFG at the nucleus].

In compounds of quadrivalent tin there is a possibility of the formation of four (sp^3 hybridisation) or six (sp^3d^2 hybridisation) equivalent bonds, which ensure equal populations of the p_x, p_y, and p_z states and as a consequence the absence of a field gradient at the ^{119}Sn nucleus. On the other hand, the upper limit of the variation of ΔE for tin(IV) compounds can be greater than for bivalent tin compounds: $\Delta E = 0-5.4$ mm s^{-1}.[1,4,10-12,17-43,70] Table 1 presents the limits of the variation of the quadrupole splitting in the Mössbauer spectra of the complexes $[R'R''R'''P(Y)]_{2(1)} . SnR_nX_{4-n}$.

Analysis of the Mössbauer spectroscopic data in Tables 1–9, combined with data for the geometrical structures[10,26,60,67,71] and the enthalpies of formation[62,63] of the complexes $[R'R''R'''P(Y)]_2SnX_4$ and the complexes of organophosphorus compounds with alkyltin halides, shows that the following factors make the main contributions to the generation of the electric field gradient at the tin nucleus and hence to the quadrupole splitting ΔE for compounds of this type[42]: (1) the geometrical configuration of the complexes (*cis–trans* isomerism), (2) the spatial configuration of the organophosphorus ligand, (3) the electron-donating capacity of the atom Y in the P=Y group and the nature of the substituent R_nX_{4-n} atom.

We shall consider in greater detail the influence of each factor on the ΔE for the compounds investigated.

Analysis of the data in Table 1 shows that, for complexes of organophosphorus compounds with tin halides, the Mössbauer parameters of only the compounds formed as a result of the electron-donating properties of the oxygen of the phosphoryl group, namely $[R'R''R'''P(O)]_2SnX_4$, and of the phosphorus atom, namely $[R'R''R'''P]_2SnX_4$, are sensitive to structural isomerism. For the *trans*-complexes of phosphoryl compounds, the quadrupole splitting varies from 0.5 to 1.6 mm s^{-1}, while for the *cis*–compounds it is as a rule less than 0.5 mm s^{-1} [the *cis*-complexes of tin(IV) chloride with phosphoryl chloride and the dichlorides of phosphoric and phosphonic acid are an exception]. A change in the geometry of the complexes $[R'R''R'''P(O)]_2SnX_4$ from *trans* to *cis* entails a decrease of ΔE by a factor of two[72,73] (subject to the condition that the $\Sigma\sigma^{ph}$ and ΣE_S for the substituents in the ligand are approximately equal). This is illustrated fairly clearly by the Mössbauer spectra of the following complexes (Tables 2 and 3): *cis*-$[(C_4H_9O)_2(SCH_3)P(O)]_2SnCl_4$ ($\Delta E = 0.41$ mm s^{-1}), *trans*-$[(n\text{-}C_3H_7O)_2(SCH_3)P(O)]_2SnCl_4$ ($\Delta E = 0.83$ mm s^{-1}), *cis*-$[(C_6H_5)_2(CH_3)P(O)]_2SnBr_4$ ($\Delta E = 0.37$ mm s^{-1}), and *trans*-$[(C_6H_5)_2(CH_3)P(O)]_2SnCl_4$ ($\Delta E = 0.68$ mm s^{-1}).

For complexes with similar enthalpies of formation (with similar values of $\Sigma\sigma^{ph}$ for the substituents at the phosphorus atom), ΔE increases with increase of the bulk of the substituents at the phosphorus atom—for example, $\Delta E = 0.46$ mm s^{-1} for *trans*-$[(C_2H_5)_2ClP(O)]_2SnCl_4$, $\Delta E = 0.83$ mm s^{-1} for *trans*-$[(n\text{-}C_3H_7O)_2(SCH_3)P(O)]_2SnCl_4$, and $\Delta E = 1.06$ mm s^{-1} for *trans*-$[(iso\text{-}C_3H_7O)_2(SCH_3)P(O)]_2SnCl_4$ (Table 2), i.e. an increase of the bulk of the groups at the phosphorus atom in the ligands $R'R''R'''P(O)$ induces an EFG at the tin nuclei both as a result of the geometrical isomerism of the complexes and the steric effect[11,25,31].

The possibility of using the ΔE for the determination of the geometrical structure of complexes of tetra-alkyltin halides with phosphoryl compounds is also indicated by the finding that the structure of the complexes $[R'R''R'''P(O)]_2 . SnR_nX_{4-n}$ ($n = 0-2$) is described satisfactorily on the basis of the point charge model[22,74]. According to this model, the overall EFG (q) can be represented by the sum of the independent contributions of each ligand[75]. Since $\Delta E \propto q$, the principle of additivity can be extended also to the quadrupole splitting and can be regarded as the sum of the partial quadrupole splittings (*PQS*) of the ligands.

Table 10 presents the values of *PQS* for certain organophosphorus ligands in the complexes $L_2Sn(CH_3)_nCl_{4-n}$, which we calculated by the method proposed previously[75,76], and the ΔE for these complexes. The Table shows that in most cases there is a satisfactory agreement between the calculated and experimental ΔE.

The Mössbauer spectra of the complexes $[R'R''R'''P]_2SnCl_4$ having the *trans*-structure also exhibit quadrupole splitting (Tables 1 and 6). However, in the Mössbauer spectra of the $[R'R''R'''P]_2SnCl_4$ series ΔE diminishes with increase of the bulk of the ligands—for example, $\Delta E = 1.02$ mm s^{-1} for *trans*-$[(n\text{-}C_4H_9)_3P]_2SnCl_4$ and $\Delta E = 0.58$ mm s^{-1} for *trans*-$\{[(CH_3)_2N]_3P\}_2SnCl_4$ (see Table 6), while the opposite behaviour obtains for the complexes $[R'R''R'''P(O)]_2SnCl_4$. The observed difference in the influence of the steric effects of the substituents at the phosphorus atom on the ΔE for the complexes $[R'R''R'''P]_2SnCl_4$ and $[R'R''R'''P(O)]_2SnCl_4$ can also be explained by the additional intramolecular interaction in $[R'R''R'''P]_2SnCl_4$ due to the d orbitals of the phosphorus atom[32,63]. With increase of the bulk of the substituent at the phosphorus atom in $R'R''R'''P$, the strength of this interaction should decrease, which should lead to a decrease of ΔE.

In the Mössbauer spectra of the complexes formed as a result of the electron-donating properties of the S and Se atoms, the quadrupole splitting is small or altogether absent, although the complexes have the *trans*-structure (Tables 1 and 7). Together with geometrical and steric factors the nature of the substituents at the phosphorus and tin atoms in the ligand and acceptor respectively influence significantly the quadrupole splitting.

Table 10. The calculated (ΔE_t) and experimental (ΔE_e) quadrupole splittings for the complexes $L_2Sn(CH_3)_nX_{4-n}$.

No.	L	n	ΔE_e, mm s^{-1}	ΔE_t, mm s^{-1}
1	$(CH_3)_3P(O)$	0	0.51	+0.22
2	$(CH_3)_3P(O)$	2	4.30	+4.32
3	$(CH_3)_2(CH_3O)P(O)$	0	0.25	−0.56 (*trans*) ; +0.28 (*cis*)
4	$(CH_3)_2(CH_3O)P(O)$	0	0.40	+0.26
5	$(CH_3)_2(CH_3O)P(O)$	1	2.20	+2.37
6	$(CH_3)_2(CH_3O)P(O)$	2	4.37	+4.39
7	$(CH_3)_2ClP(O)$	0	0.57	−0.38 (*trans*) ; +0.19 (*cis*)
8	$(CH_3)_2ClP(O)$	0	0.35	−0.34
9	$(CH_3)_2ClP(O)$	1	2.26	+2.25
10	$(CH_3)_2ClP(O)$	2	4.10	+4.28
11	$[(CH_3)_2N]_3P(O)$	0	0.69	−0.52
12	$[(CH_3)_2N]_3P(O)$	0	0.93	−0.48
13	$[(CH_3)_2N]_3P(O)$	1	2.35	+2.34
14	$[(CH_3)_2N]_3P(O)$	2	4.36	+4.36
15	$(n\text{-}C_4H_9)_3P(O)$	0	0.25	+0.16
16	$(n\text{-}C_4H_9)_3P(O)$	0	0.00	+0.14
17	$(n\text{-}C_4H_9)_3P(O)$	2	4.15	+4.25

Note. X = Br in complexes 4,8,12, and 16, while in the remaining cases X = Cl. The *cis*-structure is characteristic of complexes 1 and 15, complexes 3 and 7 consist of mixtures of *cis*- and *trans*-isomers, while the *trans*-structure is characteristic of the remaining complexes[65,66]. The partial quadrupole splittings (PQS_L) for complexes 1,3,7,11, and 15 are respectively −0.10, −0.13, −0.085, −0.12,[22] and −0.07 mm s^{-1}. The values of PQS for CH_3, Cl, and Br are 1.03,[22] 0.01, and 0.00 mm s^{-1} respectively.

Before considering the nature of the influence of the electronic effects of the substituents at the phosphorus and tin atoms on ΔE, we should point out that, as a consequence of the large number of variables determining the ΔE for the compounds investigated, Herber's rule does not hold for the complexes $[R'R''R'''P(Y)]_2SnX_4$.[77] According to this rule, the ratio of the quadrupole splitting to the isomer shift $\rho = \Delta E/\delta$ is determined by the coordination number of tin. If $\rho < 1.8$, then the tin atom is tetracoordinated, while for $\rho > 2.1$ the environment of the tin atom is octahedral or trigonal-bipyramidal. The data summarised in Table 1 show that Herber's rule is valid only for the *trans*-complexes of organophosphorus compounds with tin tetrahalides formed due to the electron-donating properties of the phosphoryl oxygen.

2. Chemical Effects

Since, like the isomer effect, the quadrupole splitting characterises the electronic structure of the Mössbauer atom, it is natural to expect that[26,31,36,41,42,47,49,51,54,77-82] the electronegativity of the ligands and the electronic effects of the substituents in the ligand will exert a definite influence on ΔE.

Fig. 5 illustrates graphically the dependence of ΔE on $\Sigma\chi_{R,X}$ for the complexes $L_2Sn(CH_3)_nCl_{4-n}$. Evidently the quadrupole splitting increases with decrease of $\Sigma\chi_{R,X}$, i.e. the decrease of $\Sigma\chi_{R,X}$ for the substituents at the tin atom in the octahedral complexes $L_2Sn(CH_3)_nCl_{4-n}$ increases the asymmetry of the p electrons at the tin nucleus. The data for the trigonal-bipyramidal complexes $LSnR_3Cl$ deviate from the correlations presented in Fig. 5, which permits the use of ΔE together with δ for the determination of the coordination number of tin in compounds of this type[26,54].

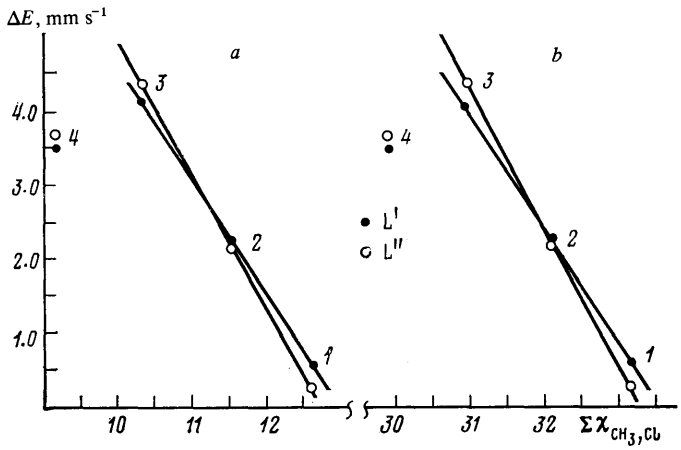


Figure 5. Relations between ΔE and $\Sigma\chi_{R,Cl}$ for the complexes $L_2Sn(CH_3)_nCl_{4-n}$, $n = 0,1,2$ [$L' = (CH_3)_2ClP(O)$; $L'' = (CH_3)_2(CH_3O)P(O)$, $n = 1$ (*1*), 1 (*2*), 2 (*3*), 3 (*4*)]; *a*) Pauling electronegativity; *b*) Mulliken electronegativity.

The influence of the substituents at the tin and phosphorus atoms on the quadrupole splitting can also be described with the aid of the substituent reaction constants σ^* and σ^{ph}.[26, 31,41,42,54,78,80,83,84] The above analysis of the correlation between the ΔE and the constants $\Sigma\sigma^*$ and $\Sigma\sigma^{ph}$ shows that they are linear. The relations between the ΔE and the $\Sigma\sigma^*$ for the complexes $L_2SnR_nCl_{4-n}$ are as follows:

$$[(CH_3)_2(CH_3O)P(O)]_2Sn(CH_3)_nCl_{4-n} (n = 0, 1, 2) \quad (9a)$$

$$\Delta E = -0.77\,\Sigma\sigma^* + 8.44\ (r = 0.995, S = 0.17, P < 0.0025, m = 4),$$
$$[(CH_3)_2ClP(O)]_2SnR_nCl_{4-n} (n = 0, 1, 2; R = CH_3, C_2H_5, C_4H_9) \quad (9b)$$

$$\Delta E = -0.71\,\Sigma\sigma^* + 7.94\ (r = 0.992, S = 0.167, P < 0.0005, m = 6),$$
$$[(n\text{-}C_4H_9)_3P(O)]_2SnR_nCl_{4-n} (n = 0, 1, 2; R = CH_3, C_4H_9, C_6H_5)$$

$$\Delta E = -0.75\,\Sigma\sigma^* + 8.28\ (r = 0.992, S = 0.24, P < 0.0005, m = 6), \quad (9c)$$
$$[(C_6H_5)_3P(O)]_2SnR_nCl_{4-n} (n = 0, 1, 2; R = C_4H_9, C_6H_5) \quad (9d)$$

$$\Delta E = 0.69\,\Sigma\sigma^* + 7.91\ (r = -0.970, S = 0.30, P < 0.001, m = 6).$$

The results show that ΔE is more sensitive to the nature of the organophosphorus ligand than δ.[32]

Since ΔE and δ vary linearly with $\Sigma\sigma^*$, there is also a linear relation between these two Mössbauer parameters[1,4,26, 41,42,54,82]:

$$[(CH_3)_2(CH_3O)P(O)]_2Sn(CH_3)_nCl_{4-n} (n = 0, 1, 2), \quad (10a)$$

$$\delta = 0.28\,\Delta E + 0.27\ (r = 0.997, S = 0.04, P < 0.0025, m = 4),$$
$$[(CH_3)_2ClP(O)]_2SnR_nCl_{4-n} (n = 0, 1, 2; R = CH_3, C_2H_5, C_4H_9) \quad (10b)$$

$$\delta = 0.32\,\Delta E + 0.31\ (r = 0.982, S = 0.08, P < 0.0005, m = 6),$$

$$[(n\text{-}C_4H_9)_3P(O)]_2SnR_nCl_{4-n}\ (n = 0, 2;\ R = CH_3, C_4H_9, C_6H_5) \quad (10c)$$

$$\delta = 0.27\,\Delta E + 0.21\ (r = 0.990, S = 0.07, P < 0.0005, m = 6),$$

$$[(C_6H_5)_3P(O)]_2SnR_nCl_{4-n}\ (n = 0, 1, 2;\ R = C_4H_9, C_6H_5) \quad (10d)$$

$$\delta = 0.32\,\Delta E + 0.21\ (r = 0.943, S = 0.14, P < 0.0025, m = 6).$$

The tendency towards a linear variation of ΔE with $\Sigma\sigma^{ph}$ for the substituents at the phosphorus atom of the ligand has also been observed[36,42,54] for the complexes of tin tetrachloride with R'R"R'"P(Y). Fig.6 illustrates graphically the relations between the ΔE and the $\Sigma\sigma^{ph}$ for the *trans*-complexes $[R'R''R'''P(Y)]_2SnCl_4$ (Y = O or LEP). We may note that the hypothesis of Phillip et al.[10] that the quadrupole splitting for the tin(IV) bromide complexes should be greater than for the tin(IV) chloride complexes does not hold for the tin tetrahalide complexes of R'R"R'"P(Y). In the vast majority of cases the upper limit of the variation of ΔE for the bromides is much smaller than for the chlorides (Tables 1–3).

For the *trans*-complexes of phosphoryl compounds with substituents at the phosphorus atom such as C_2H_5, C_6H_5, and CH_3O the quantity ΔE is almost independent of the strength of the donor–acceptor interaction (Y=O) (see Fig.6*a*, lower straight line):

$$\Delta E = 0.50 \pm 0.10\ (m = 28). \quad (11a)$$

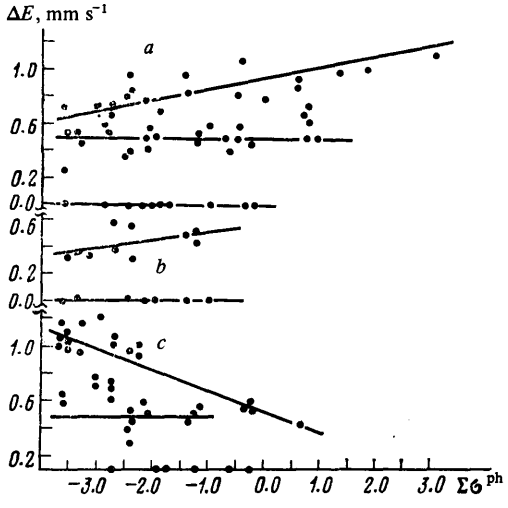


Figure 6. Relations between ΔE and $\Sigma\sigma^{ph}$ for the complexes $[R'R''R'''P(Y)]_2SnCl_4$: *a*) Y = O; *b*) Y = S; *c*) Y = LEP.

The absence of an influence by the nature of the substituents at the phosphorus atom on ΔE has been noted (see Fig.6*c*) also for certain complexes formed owing to the electron-donating properties of the phosphorus atom for Y=LEP:

$$\Delta E = 0.48 \pm 0.10\ (m = 17). \quad (11b)$$

On the other hand, for complexes containing the $(CH_3)_2N$, $(CH_3)_2CH$, and $(CH_3)_2CHO$ groups, ΔE varies approximately linearly with the $\Sigma\sigma^{ph}$ for the substituents at the phosphorus atom (Y=O):

$$\Delta E = 0.09\,\Sigma\sigma^{ph} + 0.95\ (r = 0.74, S = 0.15, P < 0.0005, m = 27). \quad (12)$$

On passing from the complexes of phosphoryl compounds to those of thiophosphoryl compounds and the complexes formed owing to the electron-donating properties of the phosphorus atom, the slope (Fig.6*c*) in the correlation equations for Y=LEP diminishes and then changes sign:

$$\Delta E = -0.15\,\Sigma\sigma^{ph} + 0.52\ (r = 0.87, S = 0.12, P < 0.0005, m = 21). \quad (13)$$

However, the behaviour of ΔE and of the isomer shift δ in the Mössbauer spectra of the $[R'R''R'''P(Y)]_2SnCl_4$ series investigated indicates in our view yet again an additional donor–acceptor interaction between the lone electron pair of the halogen atom in the acceptor molecule and the vacant *d* orbitals of the phosphorus atom in the ligand molecule in the complexes $[R'R''R'''P]_2SnCl_4$.[32,63] Comparison of the absolute slopes of the plots of ΔE against $\Sigma\sigma^{ph}$ for different series of complexes shows that the sensitivity of ΔE to the influence of the substituents in different classes of organic compounds is different and varies in the sequence R'R"R'"P > R'R"R'"P(O) > R'R"R'"P(S).

Correlation analysis of the ΔE for the Mössbauer spectra of the trigonal-bipyramidal complexes shows that here too there is a linear variation of the quadrupole splitting with $\Sigma\sigma^*$ and $\Sigma\sigma^{ph}$ and with the isomer shift[41,42]:

$$[R'R''P(O)]\,SnR_3Cl \quad (14a)$$

$$\Delta E = -0.205\,\Sigma\sigma^* + 4.087\ (r = 0.970, S = 0.047, P < 0.0005, m = 8),$$

$$\Delta E = -0.203\,\Sigma\sigma^* + 0.005\,\Sigma\sigma^{ph} + 4.085\ (r = 0.972, S = 0.045, P < 0.0005, m = 8), \quad (14b)$$

$$\delta = 0.30\,\Delta E + 0.37\ (r = 0.730,\ S = 0.06, P < 0.05, m = 6). \quad (15)$$

We may note that the dependence of ΔE on $\Sigma\sigma^*$ agrees, as regards the sign of the slope, with the analogous relation for hexacoordinate compounds [Eqns.(9) and (14)], while the literature data[78,80,83,84] indicate the opposite tendency. On the other hand, the relations between δ and ΔE agree not only as regards sign but also as regards the slopes [see Eqns.(9) and (15)].

The above expressions do not take into account the sign of the EFG. It follows from theoretical and experimental studies[85–91] on other organotin compounds that the quadrupole splitting should be positive for the *trans*-octahedral complexes and negative for the pentacoordinate complexes. The results[42] of a study of the complexes of alkyltin halides with organophosphorus ligands agree with those published previously for the *trans*-octahedral compounds[85–91]. Thus Fig.4 presents the Mössbauer spectrum of the complex $\{[(CH_3)_2N]_3P(O)\}_2Sn(CH_3)_2Cl_2$ with and without superposition of an external magnetic field at right angles to the observation axis. It follows from the resulting spectrum, in conformity with the conclusions of earlier investigations[86,87,89], that the quadrupole splitting for the above compound is greater than zero and the electric field gradient is therefore negative.

IV. THE PROBABILITY OF THE MÖSSBAUER EFFECT

In the vast majority of studies where Mössbauer spectroscopy has been used to solve various problems of coordination and organoelemental compounds, only parameters such as δ and ΔE are discussed; on the other hand, the data for the probability of the recoil-less absorption of γ-quanta (f') available in the literature are extremely limited[1,4,51,92–94]. Two studies have been published on f' in the Mössbauer spectra of complexes of tin tetrahalides with organoelemental ligands[12,92]. The limited nature of the experimental data can be explained both by the complexity of the theoretical interpretation of the results and by certain experimental difficulties[1,4,6,7].

The probability of the Mössbauer effect depends on the dynamics of the crystal lattice, i.e. on its elastic properties, and a specific model of the crystal must be selected for an examination of the dependence of f' on the macroscopic parameters of the solid. It has been shown[1,92,94] that for organometallic compounds the most convenient model of the molecular crystal is one within the framework of which it is assumed that the probability of the Mössbauer effect can be formulated to a first approximation as $f' = f'_M f'_c$, where f'_M and f'_c are the probabilities that the intramolecular and intermolecular vibrations respectively will not be excited[1].

The atomic vibrations in the molecule occur in the high-frequency range; it can be assumed that f'_M is fairly large (~1) at a low temperature and depends only slightly on the latter. The quantity f'_c, described by the Debye model[1,92], depends greatly on the temperature and makes the main contribution to the temperature variation of f'. The probability of the Mössbauer effect then increases and its temperature dependence diminishes when stronger chemical bonds are formed between individual molecules; the formation of such bonds is usually coupled with an increase of the coordination number of tin[9,95].

Thus it is evident that f' makes it possible to infer the relative strengths of the intermolecular interactions and the coordination number of the Mössbauer atom; the principal consequence of the molecular crystal model is a linear dependence of $\ln f'$ on the temperature T in the high-temperature approximation ($T > \theta/2$, where θ is the characteristic temperature of the given crystal), because f'_c is an exponential function of T. Such a dependence of the intensity and area of the Mössbauer spectrum (which depend directly on f') was demonstrated previously for different organotin compounds[51,92-94]. However, the authors[12] failed to observe a linear dependence of $\ln f'$ on T, which led them to the conclusion that the molecular crystal model is inapplicable to complexes of tin halides with organic ligands.

The results of our studies[96,97] on complexes of tin halides with organophosphorus ligands, presented in Tables 2–9, show that the probabilities of the Mössbauer effect for these systems lie within fairly broad limits: 0.15–0.58. Examination of the complexes of tin halides with mono- and bi-dentate ligands shows that the f' for these compounds are approximately the same.

The replacement of tin(IV) chloride as the acceptor by tin(IV) bromide also does not alter appreciably the probability of the Mössbauer effect, while other Mössbauer parameters (δ and ΔE) for the complexes $L_2(L')SnCl_4$ and $L_2(L')SnBr_4$ are significantly different. If the nature of the acceptor does not have an appreciable influence on f', then a tendency towards an increase of f' in the following sequence can be observed when the nature of the donor atom in the $[R'R''R'''P(Y)]_2SnX_4$ and $[R'R''P(Y)Y]_2SnX_2$ compounds investigated is altered: P : ≅ P=O > P=S (for R', R'', R''' = const.). The enthalpies of formation of the compounds vary in the same sequence[62,63].

It is noteworthy that the Mössbauer spectra of the complexes $[R'R''R'''P]_2SnCl_4$ exhibit a parallel variation of f' and ΔE, which is apparently also associated with the occurrence of an additional donor–acceptor interaction in these complexes. The highest value has been observed for the salts $[R_2P(O)O]_2SnX_2$. The probabilities of the recoil-less absorption for these substances are close to the values of f' for octahedral compounds such as SnO_2 and $BaSnO_3$.[98,99] Within the framework of the molecular crystal model, this can be accounted for by the considerable strengthening of the intermolecular bonds in such systems (compared with molecular crystals of the type L_2SnX_4) and we believe serves as additional confirmation of the octahedral structure of the given compounds[96,97].

In the case of the dithio-analogues $[R_2P(S)S]_2SnX_2$, having the octahedral bischelate structure, the probability of the Mössbauer effect is much smaller than for $R_2P(O)O]_2SnX_2$, which is apparently associated with the weaker donor–acceptor interaction in complexes formed via the thiophosphoryl sulphur[63,96,97,100,101] compared with the complexes formed via the phosphoryl oxygen.

We shall now consider the temperature variation of $\ln f'$ presented in Table 11 and in Fig. 7.[97] The data in Table 11 and Fig. 7 show that, in all the instances considered, a linear relation§ between $\ln f'(\ln c_A)$ and T holds with a satisfactory degree of reliability (a high level of significance), i.e. contrary to the data of Varnek et al.,[12] the molecular crystal model is applicable to the compounds $[R'R''R'''P(Y)]_2SnR_n \cdot X_{4-n}$ and $[R'R''P(Y)Y]_2SnX_2$, as well as other organotin compounds[9,50,92-94].

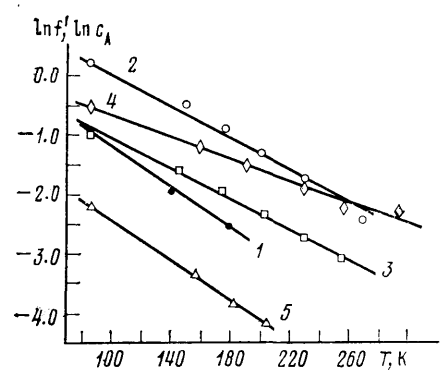


Figure 7. Temperature variation of $\ln f'$ and $\ln c_A$: 1) $\{[(CH_3)_2N]_3P(O)\}SnBr_4$; 2) $\{[(CH_3)_2N](C_6H_5)_2P(S)\}_2SnCl_4$; 3) $[(C_6H_5)_3P]_2SnCl_4$; 4) $[(n\text{-}C_4H_9)_2P(O)O]_2SnCl_4$; 5) $[(iso\text{-}C_3H_7O)_2P(S)S]_2SnCl_2$.

Table 11. The parameters of the correlations $\ln f' = 10^{-3}aT + b$ for the complexes[97].

No.	Compound	t, °C	m	$-a$	b	r	S	P	M
1	$\{[(CH_3)_2N]_3P(O)\}_2SnCl_4$	85—257	6	14.2	0.42	0.975	0.202	≤0.005	619
2	$\{[(CH_3)_2N]_3P(O)\}_2SnBr_4$	85—179	3	17.4	0.54	0.998	0.045	≤0.047	797
3	$[(C_6H_5)_2(CH_3)_2NP(O)]_2 \cdot Sn(CH_3)Cl_3$	85—266	7	16.4	0.48	0.969	0.251	<0.0005	734
4	$[(CH_3O)_3(C_6H_5)P(O)]_2SnCl_4$	85—248	6	17.4	0.60	0.962	0.291	≤0.009	633
5	$[(CH_3)_2N(C_6H_5)_2P(S)]_2SnCl_4$	85—268	6	14.9	1.66	0.994	0.099	<0.0005	783
6	$[(C_6H_5)_2ClP]_2SnCl_4$	90—232	5	27.5	3.64	0.953	0.415	≤0.013	762
7	$[(C_6H_5)_3P]_2SnCl_4$	85—253	6	12.8	0.19	0.994	0.079	<0.0005	785
8	$[(C_6H_5)_2ClP]_2SnCl_4$	85—265	7	15.7	0.46	0.974	0.283	<0.0005	510
9	$[(CH_3)_2N]_3P]_2SnCl_4$	85—235	6	14.1	0.165	0.980	0.137	<0.0005	587
10	$[(n\text{-}C_4H_9)_3P]_2SnCl_4$	85—212	5	22.5	0.65	0.982	0.206	≤0.01	665
11	DEPB.$SnBr_4$	85—229	4	21.1	0.685	0.965	0.300	≤0.04	765
12	$[(n\text{-}C_4H_9)_2P(O)O]_2SnCl_2$	85—292	6	9.05	0.21	0.988	0.096	<0.0005	658
13	$[(C_6H_5)_2P(O)O]_2SnBr_2$	85—296	8	9.26	0.29	0.947	0.205	<0.0005	713
14	$[(iso\text{-}C_3H_7O)_2P(S)S]_2SnCl_2$	85—205	4	17.8	1.38	0.995	0.085	<0.0005	616
15	$[(n\text{-}C_3H_7)_2P(S)S]_2SnCl_2$	85—229	5	20.1	0.67	0.989	0.154	≤0.0015	552
16	$[(C_2H_5)_2P(S)S]_2SnCl_2$	85—261	5	20.8	0.98	0.974	0.297	0.005	490

Note. M is the molecular weight and DEPB = 2,3-bis(diethylphosphono)butadiene. The relation $\ln c_A = 10^{-3}aT + b'$ is presented for compounds 5, 6, and 14.

§ Here c_A is the effective thickness of the absorber.

As mentioned above, according to this model one can write in terms of the high-temperature approximation[1,92]

$$\ln f' \propto \frac{3E_\gamma^2}{Mc^2} \cdot \frac{T}{k\theta^2}, \qquad (16)$$

where E_γ is the energy of the Mössbauer transition of the nucleus from the excited to the ground state, M the mass of the entire complex structural unit, c the velocity of light, k the Boltzmann constant, and θ the Debye temperature.

According to Eqn.(16), the slope of the $\ln f'(T)$ straight line is

$$a \cdot 10^{-3} = \frac{3E_\gamma^2}{Mc^2} \cdot \frac{1}{k\theta^2}. \qquad (17)$$

Hence it follows that, subject to the condition that the nature of the intermolecular bonds is the same ($\theta_M \cong$ const.), the coefficient representing the slope in the correlation equations should depend on the mass of the structural unit for different compounds. Such relations were observed previously for certain organotin compounds[102,103]. An analogous tendency towards a decrease of the absolute value of the slope with increasing mass may be noted also for certain complexes of tin halides with organophosphorus ligands (Table 11). This is manifested particularly clearly for the compounds $[R_2'P(S)S]_2SnCl_2$.

Comparison of the temperature variations of the $\ln f'$ for the tin(IV) chloride and bromide complexes shows that the probability of the Mössbauer effect for the bromides is more sensitive to temperature, since the corresponding slopes are greater in absolute magnitude than for the corresponding tin(IV) chloride compounds. The relatively small change of the slope as the nature of the acceptor is altered can be understood when account is taken of Eqn.(17). Consequently, despite the identical value of f' at 85 K, analysis of the temperature variations permits the conclusion that the tin(IV) bromide complexes have weaker chemical bonds. This conclusion is consistent with the results of studies by other methods[44,62,63]. The data presented show that, in contrast to f', the temperature variation of the probability of the Mössbauer effect is sensitive both to the nature of the ligand and to the nature of the halogen atom in the acceptor molecules. The sensitivity of the temperature variation of $\ln f'$ to the nature of the ligand varies in the following sequence: $R_2P(S)S^- \geq R'R''R'''P > R'R''R'''P(O) > R'R''P(O)O^-$ (Table 11).

Thus the study of the probability of the recoil-less absorption of gamma-quanta and its temperature variation for the complexes of tetra-alkyltin compounds and alkyltin halides with organophosphorus ligands yields interesting additional information about the properties and structures of these substances.

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Radical-Chain Reactions of Acetals in Solution

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Experimental results on the liquid-phase radical-chain reactions of acetals are summarised. Factors influencing the rate of formation, structure, and properties of free radicals generated from cyclic and linear acetals are discussed. Attention is paid mainly to the kinetics and the mechanism of the reactions of mono- and di-alkoxyalkyl radicals in solution. The relation between the structure of acetals and their reactivity towards various radicals is examined. Data are given illustrating the possibility of using homolytic liquid-phase reactions of acetals in organic synthesis. A list of 77 references is included.

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I. INTRODUCTION

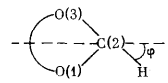
During the last 10–15 years much interesting information has been obtained on the chemistry of homolytic liquid-phase reactions of 1,3-dioxacyclanes, which has been surveyed in part[1]. This field has since been widely developed in the chemistry of acetals, and the results surveyed[1] no longer reflect the progress made in the study of radical–chain reactions of 1,1-dialkoxyalkanes, 1,3-dioxacyclanes, and related compounds.

Acetals and their hetero-analogues are successfully employed in the synthesis of various organic compounds, and are also widely used as solvents, plasticisers for polymeric materials, etc. Furthermore, linear and cyclic acetals often serve as subjects for the study of theoretical problems in organic chemistry connected with the interaction of two oxygen atoms separated by a carbon atom. The urgency of systematising and generalising data on radical reactions of acetals in the liquid phase is due to the possibility of their forming the basis of industrial processes for obtaining esters, halogenohydrin ethers, telomeric acetals, etc. from inexpensive and accessible petrochemical products.

Among the tasks of the present Review are to discuss research results on radical–chain reactions of acetals, to analyse the factors determining their reactivity, and to assess the prospects for using homolytic reactions of acetals for organic synthesis. Since an immense quantity of experimental results have been obtained on the liquid-phase oxidation of oxygen-containing organic compounds, in particular acetals, and require separate systematisation and discussion, they will not be considered in the present Review.

II. STRUCTURE OF RADICALS GENERATED FROM CYCLIC AND LINEAR ACETALS

The formation and the three-dimensional structure of mono- and di-alkoxyalkyl radicals generated from linear and cyclic acetals have been investigated by electron spin resonance spectroscopy[2–13]. Analysis of the hyperfine coupling constants of the unpaired electron with an α-hydrogen atom $a(\alpha\text{-H})$ has established[2–4,11] that in cyclic systems the deviation of the bonds of the tervalent carbon atom in dialkoxyalkyl radicals from the planar structure characteristic of alkyl and cycloalkyl radicals increases as the ring becomes smaller. The same effect has been found[13] in calculations by the extended Hückel method of the angles ϕ of distortion of the C–H bond from the plane formed by the $O_{(1)}$–$C_{(2)}$ and $C_{(2)}$–$O_{(3)}$ bonds in cyclic mono- and di-alkoxyalkyl radicals



In the 1,3-dioxacyclohex-2-yl radical the angle ϕ should be 15°, but in 1,3-dioxacyclopent-2-yl 20–25°. The dependence of $a(\alpha\text{-H})$ on ϕ can be approximated by the linear equation $a(\alpha\text{-H}) = -23.1 + 1.44\phi$.[13]

A relation has been identified[8,11] between the structure and the selectivity of formation z of cyclic dialkoxyalkyl radicals (Table 1):

$$z = \left(\frac{[N]}{[M]}\right)_{\dot{N}H_2} / \left(\frac{[N]}{[M]}\right)_{\dot{O}H},$$

where N is the dialkoxyalkyl radical, M is an alkoxyalkyl radical, and $([N]/[M])_{NH_2\cdot}$ and $([N]/[M])_{HO\cdot}$ are the concentration ratios of di- and mono-alkoxyalkyl radicals formed from acetals by the action of $\cdot NH_2$ and HO· radicals respectively.

When an acetal is attacked by different types of radicals (hydroxyl ·OH and aminyl $\cdot NH_2$), preferential formation of the 1,3-dioxacycloalk-2-yl radicals is observed[8] in both cases (Table 1). This indicates that a hydrogen atom is abstracted from the methylene or methine group between the two oxygen atoms more readily than from any other positions in the molecule. Introduction of a methyl group at position 2 or 4 facilitates formation of the corresponding di- and mono-alkoxycycloalkyl radicals (Table 1), which is more clearly evident with aminyl radicals[14].

Examination of the behaviour of cyclic formals reveals the largest difference between rate constants of homolytic cleavage of non-equivalent carbon–hydrogen bonds in 1,3-dioxolan (Table 1). Divergence from a planar structure is about the same in radicals (IX), (XIX), and (XXIV), and their rates of formation by the action of hydroxyl and aminyl radicals should not differ significantly. However, whereas radicals (XVIII) and (XXIII) give negative values of $a(\alpha\text{-H})$, −1.0 and −4.2 oersteds respectively[2], (VIII) gives $a(\alpha\text{-H}) =$ 21.5 oersteds[2,8]: i.e. the orbital of the unpaired electron is more involved in "partial" sp^3-hybridisation in (VIII). On

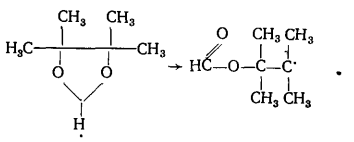
Table 1. Spectroscopic constants, relative steady-state concentrations ε, and selectivity of formation z of radicals generated from 1,3-dioxacyclanes (I)–(VII) by the action of HO· and H_2N· radicals[8].

No.	1,3-Dioxacyclane (DH) formula	No.	Radicals (D·) formula	$a(\alpha\text{-H})$, oersteds	$a(\beta\text{-H})$, oersteds	$a(\gamma\text{-H})$, oersteds	g-Factor	g-Factor ȮH	g-Factor ṄH₂	$z=\left(\frac{N}{M}\right)_{\dot{N}H}/\left(\frac{N}{M}\right)_{\dot{O}H}$
(I)	$OCH_2CH_2OCH_2$	VIII	$OCH_2CH_2O\dot{C}H$	21.5 (d)	—	1.4 (q)	2.0032	2.0	5.0	
		IX	$O\dot{C}HCH_2OCH_2$	11.4 (d)	27.2 (t)	1.5 (t)	2.0032	1.0	1.0	2.5
(II)	$OCH(CH_3)CH_2OCH_2$	X	$OCH(CH_3)CH_2O\dot{C}H$	22.0 (d)	—	1.5 (q)	2.0032	3.0	5.0	
		XI	$O\dot{C}(CH_3)CH_2OCH_2$	—	19.8 (q)	1.0 (t)	2.0030	1.5	1.0	2.5
		XII	$OCH(CH_3)\dot{C}HOCH_2$	11.4 (d)	26.4 (q)	1.4 (m)	2.0032	1.0	*	
(III)	$OCH(CH_3)CH_2OCHCH_3$	XIII	$OCH(CH_3)CH_2O\dot{C}CH_3$	—	13.5 (q) 22.5 (q)	1.0 (m)	2.0030	4.0	5.0	
		XIV	$O\dot{C}(CH_3)CH_2OCHCH_3$	—	23.5 (q)	—	2.0030	2.0	1.0	2.5
		XV	$OCH(CH_3)\dot{C}HOCHCH_3$	11.4 (d)	28.7 (q)	—	2.0030	1.0	*	
(IV)	$OCH(CH_3)CH(CH_3)OCCH_2CH_2CH_2CH_2$	XVI	$O\dot{C}(CH_3)CH(CH_3)OCCH_2(CH_2)_2CH_2$	—	20.5 (q) 28.0 (q)	—	2.0031	1.0	3.0	3.0
		XVII	$OCH(CH_3)CH(CH_3)O\dot{C}CH(CH_2)_2CH_2$	21.7 (d)	37.0 (q)	0.5	2.0029	1.0	1.0	
(V)	$OC(CH_3)_2CH_2CH_2OCH_2$	XVIII	$OC(CH_3)_2CH_2CH_2O\dot{C}H$	1.0 (d)	—	—	2.0030	2.0	4.0	
		XIX	$OC(CH_3)_2CH_2\dot{C}HOCH_2$	16.6 (d)	47.5 (t)	1.6 (t)	2.0031	1.0	1.0	2.0
(VI)	$OCH(CH_3)CH_2CH_2OCHCH_3$	XX	$OCH(CH_3)CH_2CH_2O\dot{C}CH_3$	—	14.2 (q)	—	2.0029	3.0	6.0	
		XXI	$O\dot{C}(CH_3)CH_2CH_2OCHCH_3$	—	49.5 (t) 23.2 (q)	0.5 (d)	2.0030	1.0	1.0	2.0
		XXII	$OCH(CH_3)CH_2\dot{C}HOCHCH_3$	10.4 (d)	31.2 (t)	0.5 (d)	2.0031	1.0	*	
(VII)	$OCH_2CH_2CH_2CH_2OCH_2$	XXIII	$OCH_2CH_2CH_2CH_2O\dot{C}H$	4.2 (d)	—	1.0 (m)	2.0030	1.0	2.0	1.3
		XXVI	$O\dot{C}HCH_2CH_2CH_2OCH_2$	17.2 (d)	25.2 (t)	—	2.0028	1.0	1.5	

Note. Here d = doublet, m = multiplet, q = quintet, and t = triplet. The respective sources of HO· and H_2O· radicals were[8,11] the $Ti^{III} + H_2O_2$ and $Ti^{III} + NH_2OH$ redox systems.
*Signal of radical in e.s.r. spectrum at noise level.

this basis it was suggested[8] that attainment of the transition state in the abstraction of a hydrogen atom by active hydroxyl and aminyl radicals with homolysis of the $C_{(2)}$–H bond occurs more readily in compound (I) than in (V) and (VII). This provided a satisfactory explanation of the decrease in selectivity z on passing from five-membered to six- and seven-membered 1,3-dioxacyclanes (z respectively 2.5, 2, and 1.3).[8] This effect is also responsible for a somewhat greater selectivity ($z \cong 3$) of formation of the monoalkoxyalkyl radical (XVI) than of the cycloalkyl radical (XVII) in the case of the acetal (VI), when the differences in strength of carbon–hydrogen bonds and in geometry of the resulting radicals are very great in the 1,3-dioxacyclane and cyclopentane fragments.

The e.s.r. spectra of the acetals investigated (I)–(VII) revealed no signals that could have been assigned to acyclic acyloxyalkyl radicals[2,3,8]. At 30–50 °C and also when rearrangement of cyclic dialkoxyalkyl radicals is accompanied by the formation of tertiary acyloxyalkyl radicals, however, signals from the latter are observed in the e.s.r. spectra[11]:



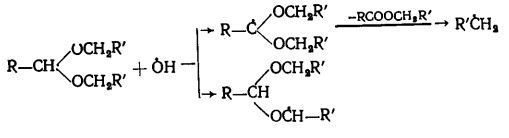
Similar observations have been made[12] on radicals generated by the photodecomposition of t-butyl peroxide. Hence cyclic dialkoxyalkyl radicals are not converted into linear acyloxyalkyl radicals at relatively low temperatures. Such rearrangement becomes appreciable above 60 °C, and causes formation of the corresponding acyclic products in the isomerisation, addition, and telomerisation of cyclic acetals[1].

Table 2. Spectroscopic constants and relative contents of radicals generated from 1,1-dialkoxyalkanes by the action of HO· and H_2N· radicals[9].

1,1-Dialkoxyalkane No.	1,1-Dialkoxyalkane formula	Radicals No.	Radicals formula	$a(\alpha\text{-H})$, oersteds	$a(\beta\text{-H})$, oersteds	$a(\gamma\text{-H})$, oersteds	[N]:[Alk], [M]:[Alk], [Alk]*
(XXV)	$CH_2(OCH_3)_2$	(XXXI)	$H\dot{C}(OCH_3)_2$	13.4 (d)	—	0.9 (sp)	2.0
		(XXXII)	$CH_2(OCH_3)O\dot{C}H_2$	17.9 (t)	—	0.9 (t)	9.0
		(XXXIII)	$\dot{C}H_3$	23.0 (q)	—	—	1.0
(XXVI)	$CH_2(OC_2H_5)_2$	(XXXIV)	$H\dot{C}(OC_2H_5)_2$	11.7 (d)	—	0.8 (m)	2.0
		(XXXV)	$CH_2(OC_2H_5)OCH_2\dot{C}H_2$	14.7 (d)	23.0 (d)	0.8 (t)	2.0
		(XXXVI)	$CH_3\dot{C}H_2$	22.4 (t)	26.9 (d)	—	1.0
(XXVII)	$CH_2(OC_3H_7)_2$	(XXXVII)	$\dot{C}H(OC_3H_7)_2$	10.5 (d)	—	0.8 (m)	1.0
		(XXXVIII)	$CH_2(OC_3H_7)O\dot{C}HCH_2CH_3$	14.4 (d)	21.0 (t)	0.8 (m)	14.0
		(XXXIX)	$CH_3CH_2\dot{C}H_2$	22.0 (t)	27.9 (t)	0.8 (m)	1.0
(XXVIII)	$CH_2[OCH(CH_3)_2]_2$	(XL)	$H\dot{C}[OCH(CH_3)_2]_2$	10.6 (d)	—	0.7 (t)	0.5
		(XLI)	$CH_2[OCH(CH_3)_2]O\dot{C}(CH_3)CH_3$	—	20.8 (m)	0.7 (t)	2.3
		(XLII)	$CH_3\dot{C}HCH_3$	21.5 (d)	24.9 (m)	—	1.0
(XXIX)	$CH_3CH(OCH_3)_2$	(XLIII)	$CH_3\dot{C}(OCH_3)_2$	—	14.8 (d)	0.8 (sp)	2.0
		(XLIV)	$CH_3C(OCH_3)O\dot{C}H_2$	17.5 (t)	—	0.5 (d)	14.0
		(XLV)	$\dot{C}H_3$	23.0 (q)	—	—	1.0
(XXX)	$CH_3CH(OC_3H_7)_2$	(XLVI)	$CH_3\dot{C}(OC_3H_7)_2$	—	14.2 (d)	0.8 (m)	12.0
		(XLVII)	$CH_3CH(OC_3H_7)O\dot{C}HCH_2CH_3$	14.4 (t)	20.8 (t)	0.8 (m)	12.0
		(XLVIII)	$CH_3CH_2\dot{C}H_2$	20.0 (t)	27.9 (t)	0.8 (m)	1.0

*Concentrations of di- and mono-alkoxyalkyl radicals N and M relative to concentration of alkyl radicals Alk.

Study of the structure and selectivity of formation of radicals from 1,1-dialkoxyalkanes (linear acetals) had established[8] simultaneous formation of mono- and di-alkoxyalkyl together with alkyl radicals by the action of hydroxyl radicals (Table 2). These last result from breakdown of relatively unstable linear dialkoxyalkyl radicals[12]:



Selectivity of formation of dialkoxyalkyl radicals increases somewhat on passing from formals (XXV)–(XXVIII) to acetals (XXIX) and (XXX). On treatment of diethoxymethane (XXVI) with the less active (than hydroxyl) aminyl radicals the selectivity of formation of diethoxymethyl radicals is approximately doubled[9]. Among the formals (XXV)–(XXVIII) increase in size and branching of the alkoxy-substituent is accompanied by an increase in relative e.s.r. signal intensity of the alkyl radicals (XXXIII), (XXXVI), (XXXIX), and (XLII), which is explained by enhancement of their stability. The concentration of alkyl radicals generated from the acetals (XXIX) and (XXX) is lower than that from the formals (XXV) and (XXVII) (Table 2), owing to the lower rate of rearrangement of tertiary than of secondary dialkoxyalkyl radicals, which is also indicated by other results[13].

III. REACTIVITY OF ACETALS TOWARDS VARIOUS RADICALS

Published data on the activity of acetals in reactions with different kinds of radicals have been obtained mainly by methods of competing reactions. The relative activities of linear, cyclic, and cyclolinear acetals towards t-butoxy-radicals have been studied[15–17], and the partial contributions by individual hydrocarbon groups determined. Table 3 summarises values of the ratio k_a/k_d for linear[15], cyclolinear[16], and cyclic[17] acetals, where k_a ($M^{-1}\ s^{-1}$) is the rate constant for abstraction of a hydrogen atom from a substrate molecule by a t-butoxy-radical

$$t\text{-BuO}^{\cdot} + QH \xrightarrow{k_a} t\text{-BuOH} + Q^{\cdot}$$

and k_d (s^{-1}) the rate constant of fragmentation of the t-butoxy-radical

$$t\text{-BuO}^{\cdot} \xrightarrow{k_d} CH_3COCH_3 + CH_3^{\cdot}\ .$$

Additive analysis of values for the ratio in Refs. 15–17 has shown that the relative partial rate constant for abstraction of a hydrogen atom from a methylene group in a hydrocarbon chain at 130 °C is 0.07–0.15 M^{-1}, and that for the methylene group $OCH(CH_3)$ is ~2.6 M^{-1}. The activation energy of detachment of a hydrogen atom from 1,1-dialkoxyalkanes by t-butoxy-radicals has been estimated[15] as lying in the range 6.5–8.5 kcal $mole^{-1}$.

Differences in reactivity between cyclolinear 2-alkoxyoxans and 2-alkoxyoxolans—(XCII)–(XCVI), (XCIX)–(CII) and (CIII)–(CVI)—are determined by the partial contributions of the alkoxyl substituents[16]. Partial contributions at 130 °C to k_a/k_d are approximately[16] 1.7, 2.8–3.0, and 0.3 M^{-1} for oxan-2-yloxy, oxolan-2-yloxy, and methoxy respectively.

Five-membered are more active than the corresponding six-membered 2-alkoxyoxacyclanes. Ring size has a similar influence among cyclic ethers, cyclic acetals[17], and their hetero-analogues[11]. The activation energy for abstraction of a hydrogen atom from 2-alkoxyoxacycloalkanes has been given[16] as ~7.0 kcal $mole^{-1}$. Abstraction of a hydrogen atom from a carbon atom adjacent to two oxygen atoms takes place most selectively[15–17] in cyclic and less selectively in linear acetals (Table 3); 2-alkoxyoxacycloalkanes occupy an intermediate position.

Table 3. Values of k_a/k_d for acetals (chlorobenzene solutions at 130 °C).[15-17]

No.	Acetal formula	k_a/k_d, M^{-1}	No.	Acetal formula	k_a/k_d, M^{-1}
(XXVII)	$(C_3H_7O)_2CH_2$	2.3	(I)	$CH_2CH_2OCH_2O$	5.2
(XLIX)	$(C_4H_9O)_2CH_2$	2.6	(LXXVI)	$CH_2CH_2OCH(CH_3)O$	6.1
(L)	$(C_5H_{11}O)_2CH_2$	2.8	(LXXVII)	$CH_2CH_2OCH[CH(CH_3)_2]O$	6.3
(LI)	(cyclo-$C_6H_{11}O)_2CH_2$	5.3	(LXXVIII)	$CH_2CH_2OCH(C_6H_{11})O$	6.4
(XXIX)	$(CH_3O)_2CHCH_3$	3.0	(LXXIX)	$CH_2CH_2OCH(C_6H_5)O$	6.6
(LII)	$(C_2H_5O)_2CHCH_3$	3.2	(LXXX)	$CH_2CH_2CH_2OCH_2O$	1.3
(XXX)	$(C_3H_7O)_2CHCH_3$	3.4	(LXXXI)	$CH_2CH_2CH_2OCH(CH_3)O$	2.7
(LIII)	$(C_4H_9O)_2CHCH_3$	3.7	(LXXXII)	$CH_2CH_2CH_2OCH(C_2H_5)O$	2.8
(LIV)	$(C_5H_{11}O)_2CHCH_3$	4.0	(VII)	$CH_2CH_2CH_2CH_2OCH_2O$	1.9
(LV)	$(C_6H_{13}O)_2CHCH_3$	4.3	(LXXXIII)	$CH_2CH_2CH_2CH_2OCH(CH_3)O$	3.1
(LVI)	$(CH_3O)_2CH-C_3H_7$	3.8	(LXXXIV)	$CH_2CH_2CH_2CH_2OCH(C_2H_5)O$	3.6
(LVII)	$(C_2H_5O)_2CH-C_3H_7$	4.0	(LXXXV)	$CH_2CH_2CH_2CH_2OOH[CH(CH_3)_2]O$	3.0
(LVIII)	$(C_3H_7O)_2CH-C_3H_7$	4.2	(LXXXVI)	$CH_2CH_2OCH_2CH_2OCH_2O$	0.7
(LIX)	$(C_4H_9O)_2CH-C_3H_7$	4.4	(LXXXVII)	$CH_2C(CH_3)_2CH_2OCH(C_2H_5)O$	2.9
(LX)	$(C_5H_{11}O)_2CH-C_3H_7$	4.6	(LXXXVIII)	$CH_2OCH_2OCH_2CCH_2OCH_2OCH_2$	2.2
(XXVIII)	(iso-$C_3H_7O)_2CH_2$	1.6	(XC)	$CHO_2H_3CH_3OC(CH_3)_2O$	5.3
(LXI)	(iso-$C_4H_9O)_2CH_2$	2.0	(XCXXXXI)	$CH_3OCH(CH_3)OCH_2CCH_2OCH(CH_3)OCH_2$	1.4
(LXII)	(iso-$C_5H_{11}O)_2CH_2$	2.3	(XCI)	$CH_3CH_2CH(CH_3)OC(CH_3)(C_2H_5)$	1.2
(LXIII)	(iso-$C_3H_7O)_2CHCH_3$	2.9	(XCII)	$OCH_2CH_2CH_2CH_2CH-OCH_3$	1.4
(LXIV)	(iso-$C_4H_9O)_2CHCH_3$	3.2	(XCIII)	$OCH_2CH_2CH_2CH_2CHOC_3H_7$	1.8
(LXVI)	(iso-$C_3H_7O)_2CH-C_3H_7$	3.5	(XCIV)	$OCH_2CH_2CH_2CH_2CHOCHCH(CH_3)_2$	2.0
			(XCV)	$OCH_2CH_2CH_2CH_2CHOC_6H_{11}$	2.6
(LXVII)	(iso-$C_4H_9O)_2CH-C_3H_7$	3.8	(XCVI)	$OCH_2CH_2CH_2CH_2CHOC_4H_9$	1.9
(LXVIII)	(iso-$C_3H_7O)_2CH-CH(CH_3)_2$	2.9	(XCVII)	$C_6H_5CH_3$	0.2
(LXIX)	(iso-$C_4H_9O)_2CH-CH(CH_3)_2$	3.2	(XCVIII)	$CH_2CH_2OCH_2CH_2O$	0.8
(LXX)	(iso-$C_5H_{11}O)_2CH-OH(CH_3)_2$	3.5	(XCIX)	$OCH_2CH_2CH_2CH_2CHOC_6H_{17}$	3.2
(LXXI)	$(CH_3O)_2CH-CH(CH_3)_2$	2.9	(C)	$OCH_2CH_2CH_2CH_2CHO(C_8H_{17}\text{-}s)$	3.1
(LXXII)	$(C_2H_5O)_2CH-CH(CH_3)_2$	3.2	(CI)	$OCH_2CH_2CH_2CH_2CHO-C_4H_9\text{-}t)$	1.8
(LXXIII)	$(C_3H_7O)_2CH-CH(CH_3)_2$	3.5	(CII)	$[OCH_2CH_2CH_2CH_2CHO]_2(CH_2)_2$	4.6
(LXXIV)	$(C_4H_9O)CH-CH(CH_3)_2$	3.7	(CIII)	$OCH_2CH_2CH_2CHOC_6H_{11}$	3.0
(LXXV)	$(C_5H_{11}O)_2CH-CH(CH_3)_2$	4.0	(CIV)	$OCH_2CH_2CH_2CHOC_8H_{17}$	4.4
			(CV)	$OCH_2CH_2CH_2CHO-C_4H_9\text{-}t)$	2.9
			(CVI)	$OCH_2CH_2CH_2CHOC_6H_{11}$	5.2

The ratio of the rate constants for abstraction by an undecyl radical of a hydrogen atom from a substrate molecule and of a chlorine atom from tetrachloromethane

$$C_{11}\dot{H}_{23} + QH \xrightarrow{k_H} C_{11}H_{24} + Q^{\cdot}$$
$$C_{11}H_{23}^{\cdot} + CCl_4 \xrightarrow{k_{Cl}} C_{11}H_{23}Cl + CCl_3^{\cdot}$$

measures the reactivity of the acetal towards the radical (Table 4).[18,19] These results show that cyclic and linear acetals are more reactive than alkylbenzenes (XCVII), (CVII), (CVIII), and carboxylic acids (CX), (CXI) by factors of ten or more.

The ratio k_H/k_{Cl} increases with increase in length of the alkoxyl substituent in 1,1-dialkoxyalkanes and on attachment of an alkyl group to the carbon atom between the two oxygen atoms. The 1,1-dialkoxyethane (XXIX), (LII), (XXX), and (LIII) are about twice as active[18] as the corresponding formals (XXV)–(XXVII) and (XLIX). This indicates that a methyl group increases the activity of the bond between hydrogen and the tertiary carbon atom in acetals relative to the secondary methylenedioxy-links in formals. The 1,1-dialkoxyalkanes (LXIII) and (LXIV), which contain isoalkoxyl substituents, are somewhat less active than the acetals (XXX) and (LIII) with straight-chain alkoxy-groups. Table 5 gives relative rate constants for detachment of a hydrogen atom by undecyl radicals from carbon–hydrogen bonds of various strengths in 1,1-dialkoxyalkanes[18].

With change in size of the heterocyclic ring activity increases from 1,3-dioxacyclohexanes (CXV), (CXVI), (XXXII) through 1,3-dioxacycloheptanes (VII), (CXVII) to 1,3-dioxocyclopentanes (I), (CXIV).[19] These results agree well with data[24] on the influence of ring size on the activity of cyclic

acetals in free-radical isomerisation, in which the limiting stage of abstraction of the hydrogen atom from the 2-carbon atom in the substrate is effected by acyloxyalkyl radicals:

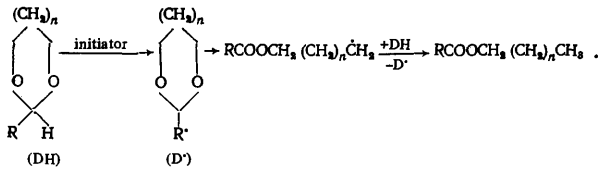
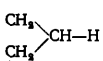
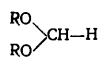
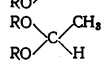


Table 4. Ratio of rate constants k_H/k_{Cl} for abstraction by undecyl radicals at 80 °C of a hydrogen atom from an acetal and of a chlorine atom from tetrachloromethane[18,19].

No.	Acetal (AH) formula	k_H/k_{Cl}	No.	Acetal (AH) formula	k_H/k_{Cl}
(XXV)	$(CH_3O)_2CH_2$	0.14	(XCVII)	$C_6H_5CH_3$	0.01*
(XXVI)	$(C_2H_5O)_2CH_2$	0.17	(CVII)	$C_6H_5CH_2CH_3$	0.02
(XXVII)	$(C_3H_7O)_2CH_2$	0.20	(CVIII)	$C_6H_5CH(CH_3)_2$	0.03
(XLIX)	$(C_4H_9O)_2CH_2$	0.24	(CIX)	CH_3COOH	0.02
(XXVIII)	$[(CH_3)_2CHO]_2CH_2$	0.16	(CX)	CH_3CH_2COOH	0.02
(LXI)	$[(CH_3)_2CHCH_2O]_2CH_2$	0.18	(CXI)	$CH_3CH_2CH_2COOH$	0.02
(LXII)	$[(CH_3)_2CHCH_2CH_2O]_2CH_2$	0.22	(CXII)	$C_4H_9OCH_3$	0.11
(LI)	$(C_5H_{11}O)_2CH_2$	0.57	(CXIII)	$(C_4H_9)_2O$	0.15
(XXIX)	$(CH_3O)_2CHCH_3$	0.31	(I)	$OCH_2CH_2OCH_2$	0.70
(LII)	$(C_2H_5O)_2CHCH_3$	0.37	(CXIV)	$OCH_2CH_2OCHC_3H_7$	0.98
(XXX)	$(C_3H_7O)_2CHCH_3$	0.40	(CXV)	$CH_2C(CH_3)_2CH_2OCH_2O$	0.22
(LIII)	$(C_4H_9O)_2CHCH_3$	0.44	(CXVI)	$CH_2C(CH_3)_2CH_2OCH(C_3H_7)O$	0.35
(LIV)	$(C_5H_{11}O)_2CHCH_3$	0.48	(XXXII)	$CH_2CH_2CH_2OCH(C_3H_7)O$	0.36
(LXIII)	$[(CH_3)_2CHO]_2CHCH_3$	0.32	(VII)	$CH_2CH_2CH_2CH_2OCH_2O$	0.35
(LXIV)	$[(CH_3)_2CHCH_2O]_2CHCH_3$	0.35	(CXVII)	$CH_2CH_2CH_2CH_2OCH(C_3H_7)O$	0.54

*From Ref. 23.

Table 5. Relative partial rate constants for abstraction by undecyl radicals at 80 °C of a hydrogen atom from C–H bonds in 1,1-dialkoxyalkanes[18].

Bond type	$10^2k_H/k_{Cl}$	Bond type	$10^2k_H/k_{Cl}$
	1.0		3.0
CH_3OCH_2-H	1.2		25.0
$-OCH(CH_3)-H$	1.7		

Such a relationship indicates that the transition state is close to the final products[25]. The change in sp^3-hybridisation of the cyclic 2-carbon atom to sp^2, which occurs during detachment of the hydrogen atom, is least advantageous with the six-membered ring, which causes a decrease in the ratio k_H/k_{Cl}. The increase in activity of the 1,3-dioxacyclanes (CXIV), (CXVI), and (CXVII) with introduction of a 2-alkyl substituent into the ring is common to five-, six-, and seven-membered acetals. This effect is less marked with 1,3-dioxacyclopentanes (I) and (CXIV) than with 1,3-dioxacyclohexanes (CXV), (CXVI), and (XXXII) and 1,3-dioxacycloheptanes (VII) and (CXVII). This is attributed[19] to greater divergence of the bonds of the tervalent carbon atom from the planar structure in the resulting 2-alkyl-1,3-dioxacyclopent-2-yl radicals than in 2-alkyl-1,3-dioxacyclohex-2-yl and 2-alkyl-1,3-dioxacycloheptyl-2-yl radicals[2,8,11] and to the stabilising effect on them of the alkyl substituent.

The activities of linear and cyclic acetals towards phenyl radicals (Table 6) have been studied[20,21] by a method of competing reactions

$$C_6H_5^{\cdot} + DH \xrightarrow{k_H} C_6H_6 + D^{\cdot}$$

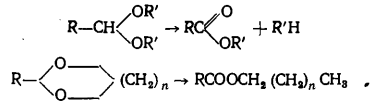
$$C_6H_5^{\cdot} + CCl_4 \xrightarrow{k_{Cl}} C_6H_5Cl + \dot{C}Cl_3$$

where DH is an acetal molecule. The qualitative pattern of relative reactivities and also the relations with the structure of the reactants and the nature of the substituents are on the whole the same as those for the reactions of acetals with undecyl radicals.

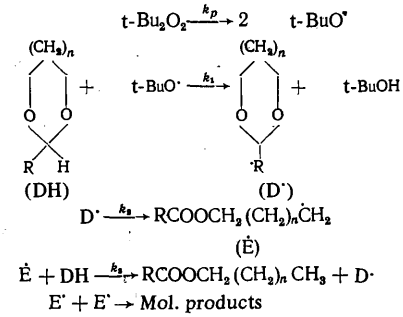
Relative partial rate constants for abstraction of a hydrogen atom from carbon–hydrogen bonds of different strengths in 1,1-dialkoxyalkanes and in 1,3-dioxacyclanes have been determined (Table 7).[20,21] The difference in activation energy for abstraction by a phenyl radical of a hydrogen atom from a 1,3-dioxacyclane and a chlorine atom from tetrachloromethane is 3.4–4.0 kcal mole^{-1}.[21]

IV. KINETICS AND MECHANISM OF HOMOLYTIC LIQUID-PHASE REACTIONS OF ACETALS

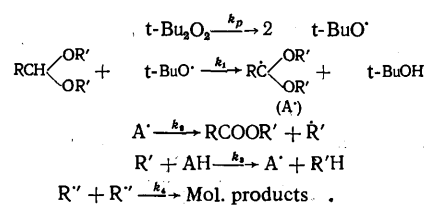
Formation of esters in the presence of radical initiators is a general reaction of linear and cyclic acetals[1,22–27]:



The reason is the greater activity in radical reactions of a carbon–hydrogen bond of a methine or methylene group located between two oxygen atoms. Kinetic study[28,29] of formation of the products has established a mechanism of isomerisation involving the sequence of primary steps—(*a*) in the case of 1,3-dioxacycloalkanes (DH)



or (*b*) in the case of 1,1-dialkoxyalkanes (AH)

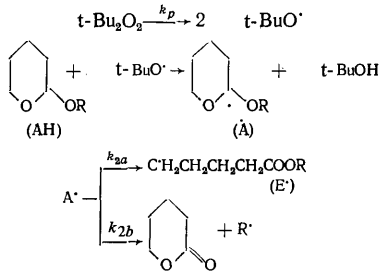


The difference in behaviour between cyclic and linear acetals is that a dialkoxycycloalkyl radical rearranges into a linear

Table 6. Ratio of rate constants k_H/k_{Cl} for abstraction by phenyl radicals of a hydrogen atom from an acetal and of a chlorine atom from tetrachloromethane[20,21].

No.	Acetal (AH) formula	$(k_H/k_{Cl})^{80°}$	No.	Acetal (AH) formula	$(k_H/k_{Cl})^{100°}$	$(k_H/k_{Cl})^{80°}$
(XXV)	$(CH_3O)_2CH_2$	2.9	(I)	$CH_2CH_2OCH_2O$	11.4	8.5
(XXVI)	$(C_2H_5O)_2CH_2$	3.1	(LXXVI)	$CH_2CH_2OCH(CH_3)O$	17.8	13.2
(XXVII)	$(C_3H_7O)_2CH_2$	3.5	(CXIV)	$CH_2CH_2OCH(C_3H_7)O$	—	13.8
(XLIX)	$(C_4H_9O)_2CH_2$	3.9	(CXIX)	$CH_2CH_2OCH(C_4H_9)O$	—	14.4
(XXVIII)	$[(CH_3)_2CHO]_2CH_2$	3.0	(CXX)	$CH_2CH_2OCH(C_6H_{13})O$	19.9	14.4
(LXI)	$[(CH_3)_2CHCH_2O]_2CH_2$	3.4	(LXXVII)	$CH_2CH_2OCH[CH(CH_3)_2]O$	—	12.8
(LXII)	$[(CH_3)_2CH(CH_2)_2CH_2O]_2CH_2$	3.8	(CXXI)	$CH_2CH_2OCH[CH_2CH(CH_3)_2]O$	—	13.1
(LI)	$(C_6H_{11}O)_2CH_2$	4.7	(CXV)	$CH_2C(CH_3)_2CH_2OCH_2O$	4.8	3.6
(XXIX)	$(CH_3O)_2CHCH_3$	4.4	(CXXII)	$CH_2C(CH_3)_2CH_2OCH(CH_3)O$	7.9	5.9
(LII)	$(C_2H_5O)_2CHCH_3$	4.8	(CXVI)	$CH_2C(CH_3)_2CH_2OCH(C_3H_7)O$	—	6.4
(XXX)	$(C_3H_7O)_2CHCH_3$	5.2	(CXXIII)	$CH_2C(CH_3)_2CH_2OCH(C_4H_9)O$	—	6.6
(LIII)	$(C_4H_9O)_2CHCH_3$	5.6	(CXXIV)	$CH_2C(CH_3)_2CH_2OCH(C_6H_{13})O$	—	7.0
(LIV)	$(C_6H_{11}O)_2CHCH_3$	6.6	(CXXV)	$CH_2C(CH_3)_2CH_2OCH[CH(CH_3)_2]O$	—	5.6
(LXIII)	$[(CH_3)_2CHO]_2CHCH_3$	4.8	(CXXVI)	$CH_2C(CH_3)_2CH_2OCH[CH_2CH(CH_3)_2]O$	—	5.9
(LXIV)	$[(CH_3)_2CHCH_2O]_2CHCH_3$	5.2	(LXXX)	$CH_2CH_2CH_2OCH(C_3H_7)O$	—	6.8
(XCVII)	$C_6H_5CH_3$	0.3	(VII)	$CH_2CH_2CH_2CH_2OCH_2O$	6.5	4.8
(CVII)	$C_6H_5CH_2CH_3$	1.1	(CXVII)	$CH_2CH_2CH_2CH_2OCH(C_3H_7)O$	—	9.5
(CVIII)	$C_6H_5CH(CH_3)_2$	1.4	(CXXVII)	$CH_2CH_2C(CH_3)_2OCH_2O$	—	3.2
(CXVIII)	$(C_3H_7)_2O$	1.2	(XXX)	$CH_2CH_2CH_2OCH_2O$	—	4.0
			(CXXVIII)	$CH_2CH_2CH_2CH_2CH_2CH_2$	—	2.7

acyloxyalkyl radical, whereas an αα-dialkoxyalkyl radical fragments with formation of an ester and an alkyl radical. These two routes are followed simultaneously in the isomerisation of cyclolinear acetals of 2-alkoxyoxans[30-32], when the 2-alkoxyoxacyclohex-2-yl radical formed is converted into an alkyl valerate or δ-valerolactone by rupture of an endocyclic or exocyclic carbon–oxygen bond:



$$(R')E^{\cdot} + AH \xrightarrow{k_3} CH_3CH_2CH_2CH_2COOR + A^{\cdot}$$

$$(R')E^{\cdot} + E^{\cdot}(R') \xrightarrow{k_4} \text{Mol. products}.$$

The variation in activity of the cyclic compounds (Table 8) depends on the size of the ring. Three competing factors—degree of hybridisation, strain in the ring, and polar effects—were taken into account[33] in considering the reactivity of these compounds with respect to isomerisation. The reactivities of the formals (I), (LXXX), (VII), (CXXIX), (XXXVI), and (CXXX) correlate with the rates of formation of carbonium ions and of decomposition of azo-compounds[33], which in view of conclusions in Ref. 34 indicates almost complete rupture of the bond in the rate-determining step. Hence the transition state must be closer in structure to the products than to the initial species. The 2-carbon atom (the reaction centre) passes from sp^3- to sp^2-hybridisation, which weakens the effect of steric hindrance in the case of 1,3-dioxolan (I), but in the reaction with seven-, eight-, and nine-membered structures (VII), (CXXIX), and (CXXX) weakens transannular interaction. When 1,3,6-trioxacyclooctane (XXXVI), in which repulsion between atoms at positions 2 and 6 is not possible, acceleration of the reaction is not observed. In the cyclohexane analogue (LXXX) the reaction is slowed down, since the almost ideal tetrahedral configuration is disrupted on passing to sp^2-hybridisation.

Table 7. Relative partial rate constants for abstraction by phenyl radicals of a hydrogen atom from carbon–hydrogen bonds in 1,1-dialkoxyalkanes at 100 °C and 1,3-dioxacyclanes at 80 °C.[20,21]

Bond in dialkoxyalkane	$(k_H/k_{Cl})^{100°}$	Bond in dioxacyclane	$(k_H/k_{Cl})^{80°}$
	0.1		
$ROCH_2$—H	0.1		0.25
ROCH(CH$_3$)—H	0.2		0.40
$(RO)_2CH$—H	1.2		0.95
$(RO)_2C(CH_3)$—H	4.0		4.2

*In a ring.

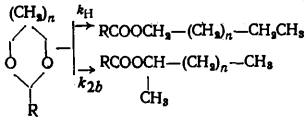
Differences in activity between the cyclic acetals (LXXVI)–(LXXIX), (LXXXI), (LXXXIII), (LXXXV), and (CXXI) are determined[17,23] by the capacity of the $C_{(2)}$–H bond for homolysis on reaction with primary alkyl radicals (Table 8). All derivatives of aliphatic aldehydes isomerise at rates exceeding the rate of isomerisation of the corresponding formals by factors of 2–3 (allowing for the number of active hydrogen atoms). The introduction of a 2-methyl group causes almost identical increases in the activity of five-, six-, and seven-membered cyclic acetals in the abstraction of a hydrogen atom by t-butoxyl,[17] undecyl,[19] and alkyl [17,23] radicals; this can be attributed to enhancement of the energy of the ground state, which is consistent with data[33] showing that increase in such energy facilitates homolysis of the bonds being broken. The slight increase in reactivity of the benzaldehyde derivative (LXXIX) is explained[35] by the non-planar structure of the 2-phenyl-1,3-dioxacycloalk-2-yl radical.

Table 8. Kinetic parameters for the isomerisation of cyclic acetals [0.3 M $(t\text{-}C_4H_9)_2O_2$].[17,23,36]

No.	Acetal formula	$10^3 \cdot k_s/k_4^{1/2}$, $M^{-1/2}\,s^{-1/2}$			
		120°	130°	140°	150°
(I)	$OCH_2CH_2OCH_2$	4.3	5.9	10.2	15.8
(LXXX)	$OCH_2CH_2CH_2OCH_2$	0.66	1.0	1.49	2.16
(VII)	$OCH_2CH_2CH_2CH_2OCH_2$	1.32	2.5	2.74	3.95
(CXXIX)	$OCH_2(CH_2)_3CH_2OCH_2$	—	5.6	—	—
(XXXVI)	$OCH_2CH_2OCH_2CH_2OCH_2$	—	1.1	—	—
(CXXX)	$OCH_2(CH_2)_4CH_2OCH_2$	—	8.0	—	—
(LXXVI)	$OCH_2CH_2OCHCH_3$	8.03	7.0	8.15	9.56
(LXXXI)	$OCH_2CH_2CH_2OCHCH_3$	1.26	1.84	2.72	5.14
(LXXXIII)	$OCH_2(CH_2)_2CH_2OCHCH_3$	2.19	3.16	4.57	6.60
(CXXI)	$OCH_2CH_2OCHCH_2CH(CH_3)_2$	5.01	7.12	10.0	14.1
(LXXIX)	$OCH_2CH_2OCHC_6H_5$	6.26	8.06	10.4	13.7
(CXXXI)	$OCH(CH_3)CH(CH_3)OCH_2$	3.1	4.0	6.4	9.0
(CXXXII)	$OCH(CH_3)CH_2CH(CH_3)OCH_2$	0.26	0.4	0.6	0.9
(CXXXIII)	$OCH(CH_3)CH_2CH_2CH(CH_3)OCH_2$	0.88	1.4	2.17	3.36

The lower reactivity of the cyclic acetals (CXXXI)–(CXXXIII) of di-secondary glycols (Table 8) than of their unsubstituted analogues is due not to change in strength of the $C_{(2)}$–H bond undergoing rupture but to differences in activity between the radicals carrying the chain[36].

2,4-Disubstituted 1,3-dioxacyclanes (Table 9) during isomerisation form esters of primary and secondary alcohols[17,37]:



Preferential formation of straight-chain esters is due[11,13,17,37] to the greater rate of formation of a secondary than of a primary radical on ring opening in a cyclic radical. Isomerisation of the 1,3-dioxans (CXXXIV), (CXXXV), and (CXXXVIII) into straight-chain esters is more selective than that of the 1,3-dioxolans (CXXXVI) and (CXXXVII) probably because the transition state is closer to the final products in the rearrangement of a six-membered than of a five-membered ring[17,37].

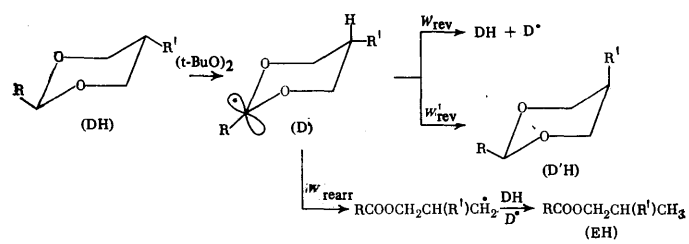
The only product of isomerisation of 4,4-dimethyl-1,3-dioxan—a formal of a primary–tertiary glycol—under the influence of t-butyl peroxide is isopentyl formate[17]. This indicates that the rate constant of rearrangement of a cyclic dialkoxyalkyl radical into a tertiary formyloxyalkyl radical exceeds the rate constant of rearrangement into a primary radical by factors of ten or more[13].

Table 9. Isomerisation of 2,4-disubstituted 1,3-dioxacyclanes[17,37].

No.	Acetal formula	k_H/k_i			ΔE^*, kcal mole^{-1}
		120°	130°	150°	
(CXXXIV)	$OCH(CH_3)CH_2CH_2OCHCH(CH_3)_2$	3.8	3.6	3.2	2.2
(CXXXV)	$OCH(CH_3)CH_2CH_2OCH_3$	6.0	5.6	4.9	2.4
(CXXXVI)	$OCH(CH_3)CH_2OCHCH_3$	1.9	1.8	1.7	1.3
(CXXXVII)	$OCH(CH_3)CH_2OCHCH(CH_3)_2$	1.8	1.7	1.6	1.2
(CXXXVIII)	$OCH(CH_3)CH_2CH_2OCHC_6H_5$	—	5.0**	—	—

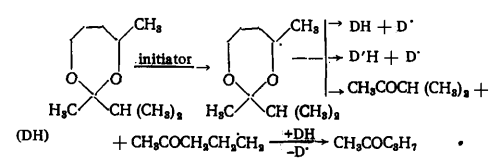
*From Ref. 40, at 135 °C.
**$\Delta E = E_H - E_i$.

In the reaction initiated by t-butyl peroxide individual stereoisomers of 2,5-dialkyl-1,3-dioxacyclohexanes not only form the corresponding esters but also undergo configurational isomerisation[11,38]:



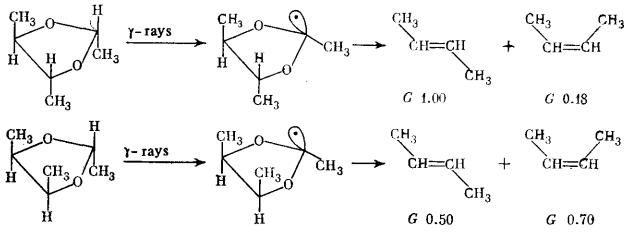
The reverse transition—from stereoisomers having an equatorial–axial arrangement of groups to isomers with a diequatorial arrangement of alkyl substituents—is also possible (DH′ → DH). It is noteworthy that at 135 °C the rate of rearrangement of 2,5-dialkyl-1,3-dioxacyclohex-2-yl radicals w_{rearr} exceeds the rate of epimerisation w'_{rev} by factors of 4–7.

Radical epimerisation of 1,3-dioxacyclanes can involve alkoxycycloalkyl radicals. Thus reaction between the low-boiling stereoisomer of 2-isopropyl-2,4-dimethyl-1,3-dioxacycloheptane (DH) and t-butyl perbenzoate at 100 °C yields methyl propyl and isopropyl methyl ketones together with the high-boiling isomer (D′H):[39]



Comparison of results in Refs. 11, 38, and 39 indicates that the ring breaks down more rapidly when dialkoxyalkyl radicals are involved. This is because rearrangement of a cyclic dialkoxyalkyl radical with formation of a carboxy-group is energetically more advantageous than is rearrangement of a cyclic monoalkoxyalkyl radical with formation of a carbonyl group[39].

1,3-Dioxacyclopent-2-yl radicals generated in aqueous medium by γ-irradiation may break down by a concerted mechanism with simultaneous rupture of two bonds[40]. Thus radiolysis of *trans*- and *cis*-2,4,5-trimethyl-1,3-dioxolans forms both *cis*- and *trans*-but-2-enes:



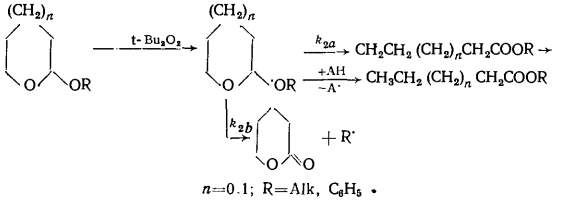
where *G* is the quantum yield. The initial *trans*-isomer gives predominantly *trans*-but-2-ene, and the *cis*-isomer gives mainly *cis*-but-2-ene.

Table 10. Kinetic parameters for homolytic reactions of 2-alkoxyoxacyclanes at 130 °C.[30]

No.	Acetal formula	k_{2b}/k_2*	k_{2a}/k_2	k_{2a}/k_{2b}	$10^3 k_2/k_4^{1/2}$, $M^{-1/2} s^{-1/2}$
(XCII)	$O(CH_2)_4CHOCH_3$	—	1.0	10.0	1.8
(XCIV)	$O(CH_2)_4CHOCH(CH_3)_2$	0.72	0.28	0.4	0.7
(CI)	$O(CH_2)_4CHOC(CH_3)_3$	1.0	—	0.4	0.2
(XCV)	$O(CH_2)_4CHO-C_6H_{11}$	0.55	0.45	0.8	1.1
(CVI)	$O(CH_2)_5CHOC_6H_{11}$	0.70	0.30	0.4	1.9

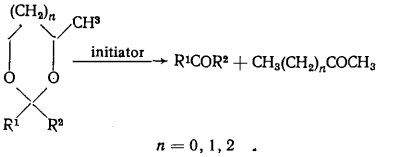
*$k_2 = k_{2a} + k_{2b}$.

The type of reaction and the relative activity of 2-alkoxyoxacycloalkanes (Table 10) depend on the structure of the alkoxy-substituent and on the size of the ring[30-32]. 2-Alkoxyoxolans (CVI) are more active than the corresponding oxans (XCV):[30]



Derivatives of primary alcohols—especially of methanol (XCII)—give predominantly the isomeric linear esters, whereas derivatives of tertiary alcohols mainly fragment with formation of δ-valerolactone[30,32]. Under otherwise similar conditions the ratio of ester to lactone is higher in the case of oxans (XCV) than with their five-membered analogues (CVI),[30] since the rate of rearrangement of cyclic dialkoxyalkyl radicals increases with ring size[11,13,41]. 2-Methoxyoxan (XCII) and 2-methyl-1,3-dioxan (LXXXI) are closely similar in reactivity. The factor determining the reactivity of cyclic acetals, independently of their structure, is obviously the presence of two oxygen atoms located α to the ruptured carbon–hydrogen bond[1].

2,2-Dialkyl-4-methyl-1,3-dioxacyclanes—cyclic ketals of primary–secondary glycols—are converted into carbonyl compounds under the influence of radical initiators, with ring cleavage at the two carbon–oxygen bonds[17,42]:



Here the reaction centre is a methine group adjacent to one oxygen atom. The reactivity of ketals, like that of acetals, is determined by the size of the ring, the presence of substituents promoting homolysis of the $C_{(4)}$–H bond, and the activity of the radicals carrying the chain.

Table 11. Kinetic parameters for the liquid-phase free-radical conversion of 1,1-dialkoxyalkanes $R^1CH(OR^2)_2$ into esters R^1COOR^2.[24-26]

Acetal No.	R^1	R^2	$10^3 k_2/k_4^{1/2}$, $M^{-1/2} s^{-1/2}$	$\lg A_2^*/A_4^{1/2}$	$E_2 - 0.5E_4$, kcal mole^{-1}
(XXVI)	H	C_2H_5	0.31	0.61	7.6±0.5
(XXVII)	H	C_3H_7	0.32	4.40	14.6±0.3
(XXVIII)	H	iso-C_3H_7	0.34	6.90	19.2±0.8
(XLIX)	H	C_4H_9	0.50	5.90	16.9±0.5
(LXI)	H	iso-C_4H_9	0.45	6.90	18.8±0.3
(L)	H	C_5H_{11}	1.19	3.40	11.7±0.3
(LXII)	H	iso-C_5H_{11}	1.01	3.90	12.8±0.3
(LI)	H	cyclo-C_6H_{11}	0.83	0.44	6.5±0.3
(XXIX)	CH_3	CH_3	1.49	3.84	12.3±0.3
(LII)	CH_3	C_2H_5	0.86	1.54	8.5±0.2
(XXX)	CH_3	C_3H_7	1.17	1.30	7.8±0.3
(LIII)	CH_3	C_4H_9	2.30	1.48	7.6±0.3
(LXIV)	CH_3	iso-C_4H_9	0.23	2.63	11.4±0.2
(CXXXIX)	CH_3	s-C_4H_9	1.41	0.73	6.6±0.3
(LIV)	CH_3	C_5H_{11}	1.96	1.08	7.0±0.8
(CXL)	CH_3	iso-C_5H_{11}	1.67	2.80	10.3±0.5
(CXLI)	CH_3	C_6H_{13}	1.23	1.64	8.4±0.5
(CXLII)	C_6H_5	C_2H_5	1.38	3.10	11.5±0.5

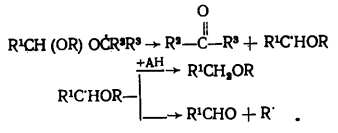
*Pre-exponential factor.

Kinetic study of the homolytic reactions of 1,1-dialkoxyalkanes[22-27] has established that their activity increases in the sequence diethoxymethane < 1,1-diethoxyethane < phenyldiethoxymethane (Table 11). Hence groups capable of delocalising the unpaired electron and thereby stabilising the intermediate dialkoxyalkyl radical enhance the reactivity of acetals.

The activity of 1,1-dialkoxyalkanes in homolytic liquid-phase reactions depends little on the size of the alkoxy-group[25].

The lower activity of 1,1-dialkoxyalkanes than of 1,3-dioxacyclanes is attributed to greater stability of carbon–hydrogen bonds in linear than in cyclic acetals, and also to the greater advantage for cyclic systems of change to an sp^2-state of the sp^3-hybridised carbon atom between the two oxygen atoms[24,25].

Formation of carbonyl compounds and ethers in the course of homolytic liquid-phase reactions is characteristic of derivatives of higher aliphatic alcohols[25]. Their rates of accumulation are lower than that of the formation of esters by factors of 2–3 and 8–10 respectively. Ethers and carbonyl compounds are formed as a result of one- and two-stage fragmentations of monoalkoxyalkyl radicals:



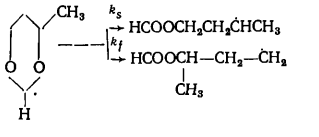
The selectivity of formation of esters diminishes on passing from derivatives of primary to those of secondary alcohols[24–26], owing to the decrease in the difference in reactivity of carbon–hydrogen bonds adjacent to one or two oxygen atoms. The difference in activation energy of rupture of such bonds by alkyl radicals is 1.0–2.5 kcal mole^{-1}.[24–26]

The rate of accumulation of ethers $R'CH_2OR$ is lower than that of formation of carbonyl compounds R'CHO by factors of 3–6. This indicates that the rate of unimolecular breakdown of monoalkoxyalkyl radicals exceeds the rate of abstraction of a hydrogen atom from a substrate molecule[24].

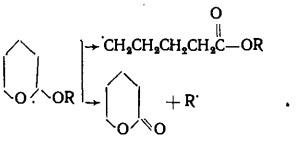
Formation of esters is also observed when reactions of 1,1-dialkoxyalkanes (XLIX) and (CXLI) are initiated by the photochemical decomposition of t-butyl peroxide (at 20 °C), but their rate of accumulation is far lower than the rate of initiation, and over a wide range is independent of the substrate concentration[43]. Under these conditions chain termination takes place mainly on dialkoxyalkyl radicals, fragmentation of which is the rate-determining stage. The rate constant of rearrangement (at 20 °C) of dialkoxyalkyl radicals $\cdot C(OR)_2CH_3$ (R = n-C_4H_9, n-C_6H_{13}) including primary alkoxy-substituents is $k_2 \approx 10$ s^{-1}.[24,43]

The influence of high pressure on the kinetics and the mechanism of the homolytic conversion of acetals into esters has been studied[11,27,30,44–47]. In the isomerisation of 2-isopropyl-1,3-dioxolan (LXXVII) the kinetic parameter $k_3/k_4^{1/2}$ remains almost unchanged with increase in pressure[11,44]. The reason is that abstraction of a hydrogen atom by primary alkyl radicals is only slightly accelerated with increase in pressure (this effect is more typical of secondary and tertiary radicals[48]), while recombination, governed by the rate of interaction of radicals in the cage, may be enhanced[44].

In the isomerisation of 4-methyl-1,3-dioxan (CXXXV) the chain is carried mainly by secondary alkyl radicals, and increasing the pressure to 7500 atm increases $k_3/k_4^{1/2}$ by factors of 2.0–2.5.[11,45] The selectivity of formation of a straight-chain ester in the isomerisation of 4-methyl-1,3-dioxolan increases with pressure, for the transition state is closer to the initial state along the reaction coordinate for the formation of a secondary than of a primary alkyl radical:

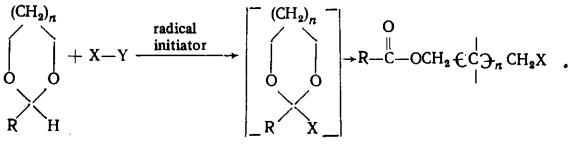


The stage of rearrangement of the 4-methyl-1,3-dioxacyclohex-2-yl radical differs little in volume of activation depending on whether a primary or a secondary acyloxyalkyl radical is formed: $\Delta V_{sf}^{\neq} \approx 3$ cm^3 mole^{-1}.[45] The direction of homolytic transformation of 2-alkoxyoxans is more noticeably influenced by pressure[30,46,47], rise in which increases the proportion of δ-valerolactone relative to the ester. The explanation is that rearrangement in both directions is slowed down[30,46], but the ring-opening rate constant is more strongly lowered:



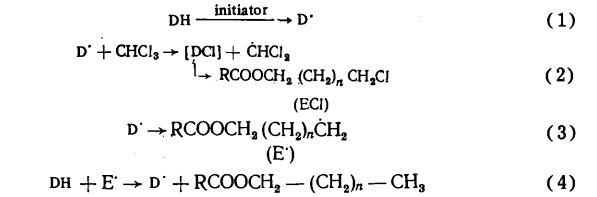
In conversion of the 1,1-dialkoxyalkanes (LXI) and (LXIV) into esters[27] the ratio of the rates of formation of isobutyl acetate and formate increases with pressure, as a consequence of the difference in reactivity towards homolytic cleavage between the secondary and tertiary carbon–hydrogen bonds in (LXI) and (LXIV). This agrees well with data showing that rise in pressure accelerates more strongly the reaction that takes place more rapidly under normal conditions[49,50].

There is much published information[1,38,51–56] indicating that 1,3-dioxacyclanes are converted under the influence of radical initiators in the presence of halogenating agents X–Y (chlorine, *N*-bromosuccinimide, polyhalogenoalkanes) into the corresponding halogenated carboxylic esters:



Formation of the latter involves[1,51–53] an intermediate unstable[53] cyclic dialkoxyalkyl halide, which rapidly isomerises into the corresponding halogenated ester. Isomerisation of the halide entails intramolecular nucleophilic substitution as a result of attack by an X^- anion at a carbon atom attached to an oxygen atom. The photolysis of optically active 2-methyl-4-phenyl-1,3-dioxolan in the presence of trichlorofluoromethane, sensitised by benzophenone, yields α-chlorophenethyl acetate with complete inversion of configuration[5].

When 1,3-dioxacyclanes undergo homolytic isomerisation in halogenoalkanes (tetrachloromethane, chloroform, bromotrichloromethane, etc.), formation of esters is accompanied by that of halogenated carboxylates[38,54–57], the latter by chain transfer to the halogenoalkane[54]. Kinetic study of the accumulation of chloroesters in chloroform suggested[38,55–57] for their formation the mechanism



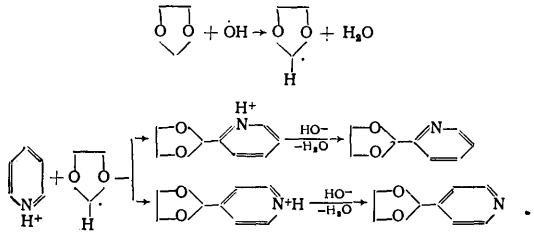
The cyclic dialkoxyalkyl radical formed is consumed in two ways: bimolecular abstraction of a chlorine atom from chloroform gives an unstable[53] 2-chloro-1,3-dioxacyclane DCl, which under the reaction conditions undergoes unimolecular conversion into the chloroester; and unimolecular rearrangement (3) into linear acyloxyalkyl radicals, which then abstract a chlorine atom from chloroform (5), finally gives the chloroester. The relative contributions of reactions (2) and (5) to

the kinetics of accumulation of the chloroester depend on the temperature[38]: at 130 °C (with t-butyl peroxide as initiator) the chloroester accumulates by both reactions, whereas at 80 °C (initiator benzoyl peroxide) reaction (2) is the chief pathway for the formation of ECl; unchlorinated esters are not found[38].

The rate-determining stage is rupture of a carbon–hydrogen bond by a dichloromethyl radical[38]. Termination takes place on such radicals. The reactivity of 1,3-dioxacyclanes towards conversion into chlorinated esters has been studied[38, 55–57]. Values of the kinetic parameter $k_3/k_4^{1/2}$, which characterise the activity of acetals towards the dichloromethyl radical at 80 °C, show[38] that it is comparable with their reactivity towards alkyl radicals only at 120–130 °C. The reason given[38] for the enhanced reactivity of dichloromethyl radicals is that a carbon–hydrogen bond is stronger in dichloromethane than in the methyl group of a normal hydrocarbon by 1.5–2.0 kcal mole^{-1}. [58,59] The nature of the substituent has little effect on the strength of the ruptured $C_{(2)}$–H bond.

Results fully consistent with these conclusions have been obtained for the conversion of 1,3-dioxacyclanes into chloroesters in the presence of 1,1,1-trichloroethane. Dichloromethyl and 1,1-dichloroethyl radicals show the same tendency to abstract a hydrogen atom. The presence of two halogenating agents[60] (e.g. tetrachloromethane with *N*-bromosuccinimide or with bromotrichloromethane) leads to parallel formation of bromo- and chloro-esters. Preferential formation of the former is attributed[60] to greater stability of the carbon–chlorine bond.

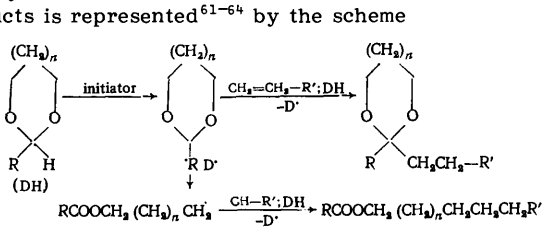
A hydrogen atom located between two oxygen atoms in 1,3-dioxolan can be replaced by a pyridine residue[61]. Thus reaction between protonated pyridine and 1,3-dioxolan in the presence of iron(II) sulphate together with hydrogen peroxide to supply hydroxyl radicals gives 2- and 4-(1,3-dioxacyclopent-2-yl)pyridines:



The 2-isomer is formed preferentially, which is on the whole characteristic of homolytic substitution of protonated heteroaromatic bases under the influence of nucleophilic carbon-centred radicals.

V. RADICAL ADDITION OF ACETALS TO ALK-1-ENES

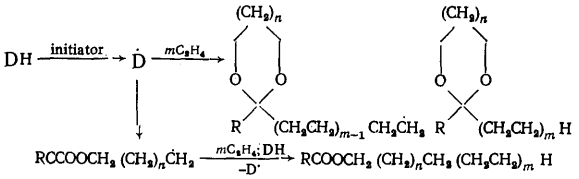
Addition of 1,3-dioxacyclanes to terminal alkenes (hexene, octene, ethylene) yields the corresponding 2-alkylated 1,3-dioxacyclanes and esters[62–70]. The formation of addition products is represented[61–64] by the scheme



$n = 0, 1, 2$; R′ = H, C_4H_9, or C_6H_{13}; R = H, or Alk.

The relative proportions of linear and cyclic products depend[41,61] on the temperature and the structure of the dioxacyclane. Below 50 °C the main products are 2-alkyl-1,3-dioxacyclanes. With rise in temperature the yield of esters increases. Increase in ring size has a similar effect, which is explained[61] by increase in the rate of unimolecular rearrangement of dialkoxyalkyl radicals on passing from five- to seven-membered rings[11,13]. The yield of cyclic products increases on passing from formals to acetals, owing[61,62] to the lower rate of unimolecular rearrangement of tertiary than of secondary dialkoxycycloalkyl radicals[11,13,41]. Substituents capable of delocalising the unpaired electron at position 2 in the 1,3-dioxacyclane somewhat increase the yield of 2-alkyl-1,3-dioxacyclane[61].

Two series of products—ester telomer-homologues and 2-alkyl-1,3-dioxacyclanes—have been identified[65–70] in the radical telomerisation of ethylene by cyclic acetals at 50° to 150 °C. The mechanism



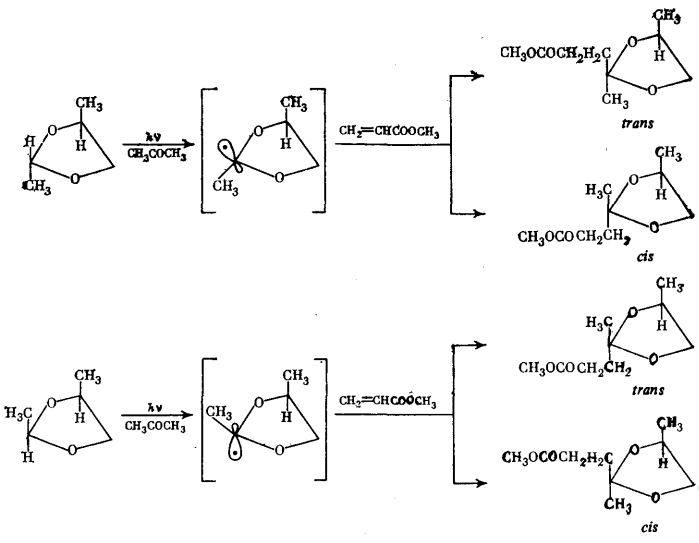
was suggested[65–70] for the formation of these products. The cyclic dialkoxyalkyl radical adds to ethylene or else gives a linear acyloxyalkyl radical by intramolecular rearrangement. The latter adds to ethylene to form esters. The values found[65–68] for the partial chain-transfer constants ($C_n \cong 0.1$ to 0.3) characterise 1,3-dioxacyclanes as telogens of medium activity. The fact that C_n is independent of the number T_n of monomer units already added to the growing radical indicates that the 1,3-dioxacyclane substituent exerts no polar effect.

Telomerisation of a five-membered cyclic formal, 1,3-dioxolan, is accompanied by formation of a new series of products, 2-alkyl-2-butyl-1,3-dioxolans[65,69], which is attributed[69] to rearrangement of the growing radical T_n ($n = 2$) with 1,5-migration of a hydrogen atom. Such transfer is made possible by an unstrained transition state having a six-membered ring structure[65,69].

The radical telomerisation of ethylene by 2,4-dimethyl-1,3-dioxan (VI) (in the presence of dicyclohexyl peroxodicarbonate at 50 °C) yields stereoisomeric 2-alkyl-2,4-dimethyl-1,3-dioxans[71]. Isomers having an axial—equatorial arrangement of methyl groups are formed preferentially. This is assumed[71] to be due to the shielding effect of the axial $H_{(1)}$–$H_{(6)}$ atoms or to the non-planar structure[11,14,23] of the 2,4-dimethyl-1,3-dioxacyclohex-2-yl radical (XX). The telomerisation of ethylene by 4-methyl-1,3-dioxolan (benzoyl peroxide at 80 °C) also yields predominantly *trans*-2-alkyl-4-methyl-1,3-dioxolans, which is attributed[72] to the same causes[71].

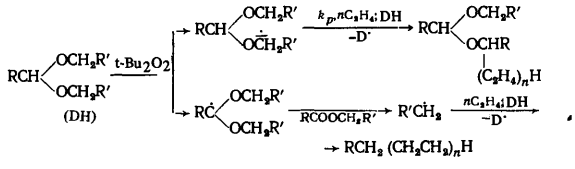
Photochemical addition of *cis*- or *trans*-2,4-dimethyl-1,3-dioxolan to methyl acrylate (at −78 °C) gives a mixture of geometric isomers, in which that with a *cis*- or *trans*-

arrangement of the methyl groups respectively predominates[73]:



Such stereoselective addition of methyl acrylate is attributed[73] to the pyramidal structure of the 2,4-dimethyl-1,3-dioxacyclopent-2-yl radical, which under the reaction conditions (−78 °C) partly retains the original structure. With rise in temperature above 20 °C the *cis*-dimethyl isomer is formed preferentially. Inversion of the pyramid of the tervalent carbon atom apparently occurs readily with rise in temperature, and the stereoselectivity of addition is determined by the presence of the 4-methyl group.

The radical telomerisation of ethylene by 1,1-dialkoxyalkanes[74–77] gives unsymmetrical linear acetals formed by the addition of monoalkoxyalkyl radicals to ethylene; esters and unsaturated hydrocarbons are also formed. The latter results from addition to ethylene of fragmentation products from the 1,1-dialkoxyalkanes. The telomerisation of ethylene by 1,1-dialkoxyalkanes initiated by t-butyl peroxide is represented[74–77] by the scheme

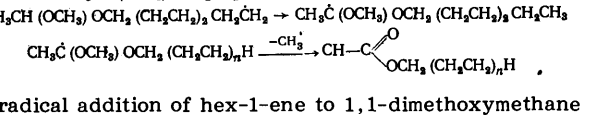


Products of the addition of dialkoxyalkyl radicals to ethylene are not detected, for linear radicals of this type are unstable[13]. Even at 20 °C they break down unimolecularly to form esters and alkyl radicals[9,23,76,77].

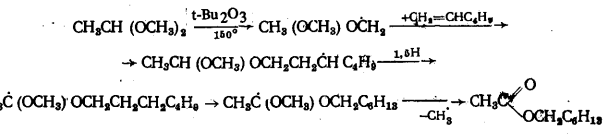
The radical telomerisation of ethylene by 1,1-dialkoxyalkanes is characterised[76,77] by partial chain-transfer constants $C_n = k_n/k_p$; for example, the values of these constants for diethoxymethane are[76]

$$C_1 = 0.18 \pm 0.02;\ C_2 = 0.19 \pm 0.02;\ C_3 = 0.19 \pm 0.02 \text{ (Ref.76)}.$$

Hence linear acetals are comparatively ineffective reaction-chain carriers and are telogens of moderate activity. Since C_n is independent of the number n of monomer units, the acetal radical exerts no polar effect on chain transfer[76]. In the telomerisation of ethylene by 1,1-dimethoxymethane not only unsymmetrical linear acetals but also propyl and heptyl acetates (n = 1, 3) have been identified, though pentyl acetate (n = 2) was not detected in the reaction mixture[76,77]. The selective formation of propyl and heptyl acetates is explained[76,77] by the novel process (for this reaction) of rearrangement of the first and third growing radicals (n = 1, 3) with 1,5- and 1,9-migration of a hydrogen atom:



The radical addition of hex-1-ene to 1,1-dimethoxymethane initiated by the thermal decomposition of t-butyl peroxide (at 150 °C) is also accompanied by rearrangement with 1,5-migration of a hydrogen atom[76,77]:



The ease with which such migration takes place is due to the unstrained character of the transition state, whose geometry is similar to that of the cyclohexane ring.

---o0o---

On the whole the above features of homolytic liquid-phase reactions of cyclic and linear acetals and related compounds are due to the presence of carbon–hydrogen bonds activated by oxygen atoms. The selectivity of formation of dialkoxyalkyl radicals and their reactivity towards various reagents mainly determine the rate and direction of transformation of acetals in solution.

The information surveyed on the homolytic reactions of acetals in solution demonstrates the prospects for using such reactions to generate substituted carbon-centred radicals and employing them in organic synthesis.

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The Crystal Structures of Potentially Tautomeric Compounds

N.G.Furmanova

Data on the structures of potentially proto-, metallo-, and carbono-tropic compounds, obtained mainly by X-ray diffraction, are surveyed. The results of neutron and electron diffraction studies have also been partly used. It is shown that a characteristic feature of all the systems considered is the formation of hydrogen or secondary bonds ensuring the contribution of both possible tautomeric forms to the structure. Systematic consideration of the experimental data leads to the conclusion that there is a close relation between the crystal structure and the dynamic behaviour of the molecules in solution and that secondary and hydrogen bonds play a significant role in the tautomeric transition.
The bibliography includes 152 references.

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I. INTRODUCTION

Among the physical methods for the investigation of molecular structure, X-ray diffraction analysis, which makes it possible to determine the structure objectively without any *a priori* models, occupies the principal place. Systematic consideration of the enormous amount of experimental data obtained by this method shows that in the crystals of the vast majority of organic and organometallic compounds the distances between atoms of the given kind can be divided into two groups: the distances between atoms joined by a chemical bond (they are characterised by the sum of the covalent radii) and the distances between atoms not linked by chemical bonds, the shortest of which are usually close to the sums of the van der Waals radii. Since the van der Waals radii are greater by ~0.8 Å than in the covalent radii, in the spectrum of interatomic distances there is a "gap" separating valence distances from non-valence distances.

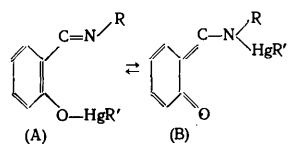
However, in the last few years an increasing number of interatomic distances occupying precisely this gap have been observed. The accumulation of experimental data on structures of this type suggests the possibility of applying X-ray diffraction not only to the determination of the geometrical characteristics of the initial substances and reaction products but also to the solution of certain problems concerning chemical processes. This field is undergoing an increasing development at the present time. In particular, systematic studies are being prosecuted in Switzerland in Bürgi's group[1]. Burgi believes that any chemical reaction involving the dissociation of some bond and the formation of others should be characterised by structural data demonstrating a continuous transition between the covalent bond and the van der Waals contact.

Bürgi and coworkers carried out X-ray diffraction studies on a series of alkaloids and related compounds containing a tertiary amino-group and a carbonyl group. A set of these structures, in which a correlation has been found between the shortening of the intramolecular N...C contact and the breakdown of the coplanarity of the covalent bonds involving the C atom, constitutes a model of the nucleophilic addition to the carbonyl group involving the formation of an intermediate with a tetrahedral carbon atom. An analogous correlation has also been observed for the O...C=O contacts[2].

This review deals with the application of X-ray diffraction analysis to the study of elemento- and proto-tropic systems.

II. DERIVATIVES OF SALICYLALDEHYDE

In the determination of the crystal structures of tautomeric (or potentially tautomeric) compounds the problem of which of the two possible molecular forms exist in the crystal arises in the first place. Thus Minkin and coworkers demonstrated[3] by electronic absorption and luminescence spectroscopy that phenyl- and methylmercury derivatives of *o*-hydroxyarylaldimines exist in solution in the form of an equilibrium mixture of benzenoid and quinonoid tautomers, whose ratio varies with temperature and solvent polarity:



(A) (B)

X-Ray diffraction analysis showed[4] that in the crystal the phenylmercury *N*-methylsilicylideneaminate molecule is an *N*-derivative with the *cis*-configuration relative to the C(2)–C(3) exocyclic bond (Fig.1). This configuration is favourable for intramolecular coordination and the Hg...O distance [2.44 (3) Å] in this molecule is indeed smaller by ~0.5 Å than the sum of the van der Waals radii of these atoms, which indicates a coordination interaction (a secondary Hg...O bond). Coordination leads to the breakdown of the linearity of the N–Hg–C fragment: the angle between the covalent bonds involving the Hg atom is 167(1)°.

The detection of the Hg–N covalent bond, which has the usual length, implies that the molecular structure is best described in terms of the quinonoid form B, but the strong

intramolecular Hg...O interaction indicates a considerable contribution of the benzeneoid structure A also. The interatomic distances in the salicylideneaminate ligand can therefore be intermediate between the distances in A and B, but the accuracy with which the location of the carbon atoms can be specified in the presence of a heavy metal such as mercury is insufficient for the consideration of such fine structural details.

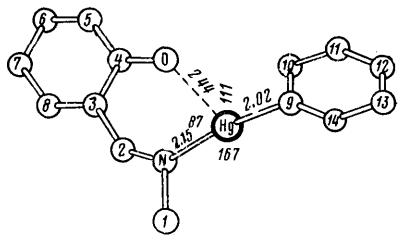


Figure 1.

In contrast to this structure, in the dimethyltin *N*-(2-hydroxyphenyl)salicylideneaminate molecule[5] the Sn...O distance in the salicylideneaminate chelate ring [2.130(7) Å] is somewhat shorter than the Sn–N distance [2.225(8) Å], which indicates that the benzenoid *O*-form predominates (Fig.2). The distribution of bond lengths in this chelate ring is also consistent with the above treatment. At the same time, the shortening of the C–O bond to 1.30(1) Å compared with the C–O bond in the hydroxyphenyl fragment of the same molecule [1.35(1) Å] and with the value usual for phenols (1.38 Å) as well as the shortening of the C–C(=N) bond to 1.45(1) Å indicate a contribution of the quinonoid *N*-form.

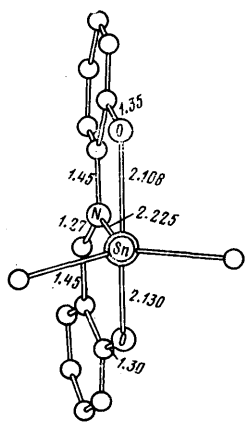


Figure 2.

In *N*,*N'*-ethylenebis-salicylideneaniline[6] (Fig.3) and *N*-*N'*-(*o*-phenylene)bis-salicylideneaniline[7] the salicylideneamine fragment exists in the benzenoid form, although the O–H...N intramolecular hydrogen bond, analogous to the secondary Hg...O bond in the phenylmercury derivative, ensures some contribution (albeit very small) of the quinonoid structure. In transition metal complexes the salicylideneaminate ligand has an intermediate structure, all its interatomic distances being close to the lengths of aromatic bonds (see, for example, Lingafelter and Braun[8]).

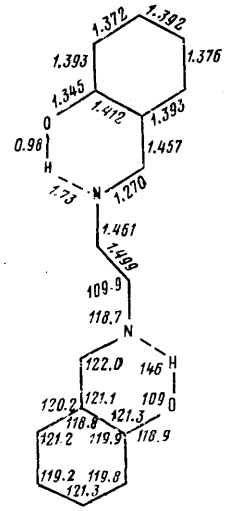


Figure 3.

The structure of the salicylaldehyde complex of diethylthallium[9] is also best described in terms of the benzenoid form: the Tl–O(1) distance involving the phenolic oxygen atom (2.46 Å) is much shorter than Tl–O(2) (2.61 Å); the C(1)–O(2) bond (1.23 Å) is close to the normal double bond and the C(2)–O(1) bond (1.32 Å) is close to a single bond.

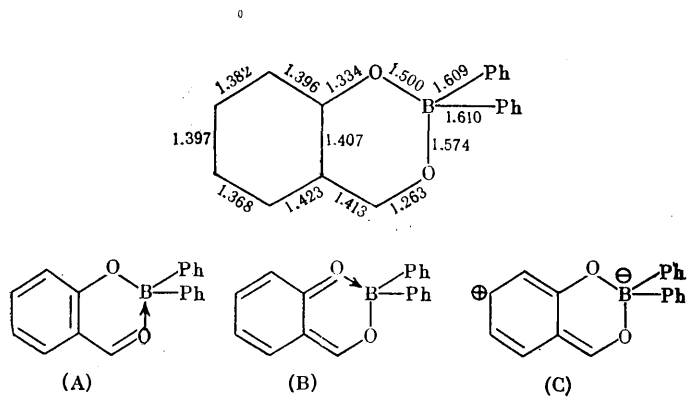


Figure 4.

The salicylaldehyde complex of diphenylboron has an analogous structure[10] (Fig.4). The B–O bond lengths in this molecule are significantly non-equivalent: 1.500 and 1.574 Å, which leads to the conclusion that the contribution of the benzenoid form A to the structure predominates, but even the shorter of these bonds is somewhat longer than

the usual value 1.477 Å. The absence of heavy atoms from this molecule made it possible to determine the structure with a higher accuracy and to discover the real distribution of bond lengths, indicating a significant contribution of the three resonance forms—benzenoid (A), *o*-quinonoid (B), and *p*-quinonoid (C)—to the structure.

A similar distribution of bond lengths has been found in the *o*-vanilline molecule[11]†, where a strong intramolecular hydrogen bond was observed (Fig.5*a*), but, judging from the C–O and C–C (exocyclic) bonds, the contribution of the benzenoid form is in this case somewhat greater than in the boron compound. The bond lengths in the aldehyde group are significantly different from the corresponding values in 2-nitrobenzaldehyde[13] (Fig.5*b*), where there is no hydrogen bond. Similar structures are characteristic also of the salicylic acid molecule (determined by X-ray diffraction[14] and neutron diffraction[15]) and the 2-amino-3-methylbenzoic acid molecule[16].

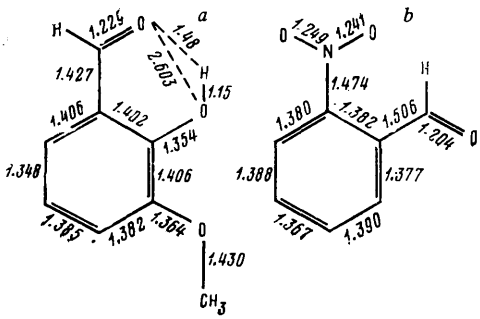


Figure 5.

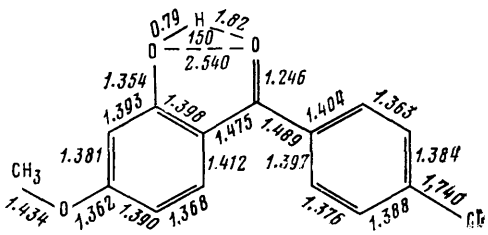


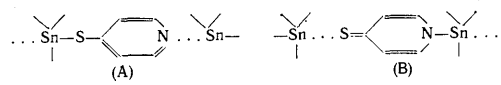
Figure 6.

The quinoid form makes a significant contribution to the structures of 2-hydroxy-4-methoxybenzophenone[17] and 4-chloro-2-hydroxy-4'-methoxybenzophenone[18] (Fig.6), where a six-membered ring is also formed as a result of an intramolecular hydrogen bond. In the 2,4-dihydroxybenzophenone crystal[19] there is an intermolecular as well as an intramolecular hydrogen bond, so that both the *o*-quinonoid and *p*-quinonoid forms should contribute to the resultant structure. As a result of this, although the C=O, C–O, and C–C (exocyclic) bonds are similar in all three structures, in the benzene ring of the last structure only one bond is distinctly shortened, namely that which should be double in both *o*- and *p*-quinonoid structures.

†The structure of the unsubstituted salicylaldehyde was investigated only in 1953 [12] and the accuracy of its determination is insufficient for the consideration of fine structural details.

III. HYDROXY-, MERCAPTO-, AND AMINO-PYRIDINES

Potentially metallotropic compounds can also form systems with intermolecular coordination in the crystalline state. In particular, the triphenyltin derivative of 4-thiopyridone has such a structure. In principle, its structure can be described in terms of one of two forms: the mercaptopyridine form (A), or the thiopyridone form (B), or a resonance hybrid of forms (A) and (B) with equal contributions by each:



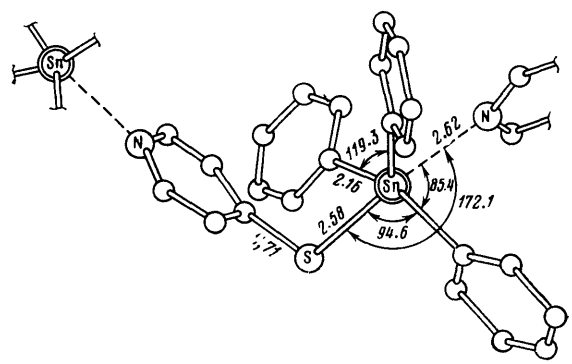


Figure 7.

X-Ray diffraction analysis showed[20] that the crystal is made up of infinite zig-zag chains (Fig.7) with trigonal-bipyramidal coordination of the tin atom. The Sn–S and Sn–N distances are longer than the corresponding single bonds but are appreciably shorter than the normal van der Waals contacts, which indicates a strong intermolecular coordination. However, the contributions of the two limiting forms to the given structure are nevertheless not the same. The Sn–S distance (2.58 Å) exceeds the length of the single bond by only 0.14 Å (the sum of the covalent radii is 2.44 Å [21]), while the Sn...N distance (2.62 Å) exceeds the single bond length by 0.52 Å (the sum of the covalent radii is 2.10 Å). Furthermore, the S–Sn–C valence angles (the average angle is 94.6°) are greater than the N...Sn–C angles (85.4°) and smaller than the ideal value for a trigonal bipyramid (90°), i.e. there is a tendency towards the retention of a tetrahedron at the Sn atom with participation of the S atom. Thus the structure of the test compound in the crystal is best described in terms of the mercaptopyridine form (A), although the contribution of form (B) is considerable. Apart from the lengthening of the Sn–S bond already mentioned, this is indicated by the shortening of the S–C bond to 1.71 Å compared with the normal value (1.78 Å). The triphenyl-lead derivative of 4-thiopyridone has a very similar structure[22].

In contrast to these compounds, which are S-derivatives in the crystal, the isothiocyanate $(CH_3)_2Sn(NCS)_2$ [23] and $(CH_3)_3SnNCS$ [24] are N-derivatives: their Sn–N bond lengths are respectively 2.14 and 2.15 Å, while the Sn...S distances are 3.20 and 3.13 Å.

For both salicylaldehyde and pyridone (hydroxypyridine) derivatives, a considerable similarity of the crystal structures of the metallotropic compounds and their prototropic analogues has been observed. Unfortunately, unsubstituted 4-thiopyridone has not been investigated by X-ray diffraction, but the structures of a series of 4-pyridone derivatives are known. Comparison of the structures of the 2,3,5,6-tetrachloro-derivative (I) [25] and the 3,5-dichloro-2,6-dimethyl derivative (II) [25,26] is of greatest interest. In both compound (I) and compound (II) hydrogen bonds connecting the molecules into infinite chains have been discovered, but compound (I) is a hydroxypyridine tautomer, while compound (II) is a pyridone tautomer (Fig.8).

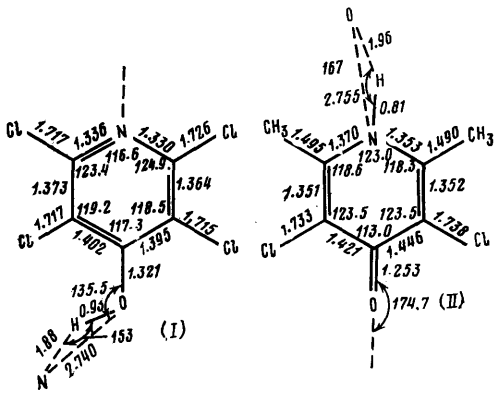


Figure 8.

The main evidence for this comes from the location of the hydrogen atoms in the two structures: the O–H...N hydrogen bond with an O–H distance of 0.93 Å, an H...N distance of 1.88 Å, and an O–H...N angle of 153° is formed in compound (I); in compound (II) the N–H...O bond has an N–H length of 0.81 Å, an H...O length of 1.96 Å, and an N–H...O angle of 167°. The lengths of the valence bonds and the angles also indicate the presence of hydroxy- and oxo-tautomers. It is known (see, for example, Singh[27]) that in six-membered heterocycles the endocyclic bond at an N atom linked to an H atom is much greater (>120°) than at an N atom not linked to an H atom (<120°), which agrees with the values observed for structures (I) and (II). Furthermore the C–O bond length in compound (II) approaches the value of 1.215 Å in aldehydes and ketones[28], while in compound (I) it is close to the value (1.36–1.38 Å) characteristic of aromatic alcohols, although the former is appreciably lengthened while the latter is actually shortened. Finally the bonds in the ring of compound (II) indicate an appreciable localisation, while in compound (I) they are close to the corresponding values for pyridine (the N–C and C–C bond lengths are 1.340 and 1.394 Å respectively[28]).

The stabilisation of the hydroxypyridine form of compound (I) is due to the presence of electron-accepting substituents in the α-position relative to the N atom: by increasing the acidity of the pyridone form and reducing the basicity of the N atom in the hydroxypyridine form, these substituents promote a shift of the tautomeric equilibrium towards the hydroxypyridine form[29]. However, one should note that, although both the intermolecular coordination involving the metal atom and the hydrogen bond lead to the generation in the crystal of forms intermediate between the two limiting forms (which is manifested particularly by the lengthening of the C=O bonds and the shortening of the C–O bonds in pyridone derivatives), the structure of the organotin derivative of 4-thiopyridone is much closer to the resonance hybrid of the two forms than all the known structures of organic analogues.

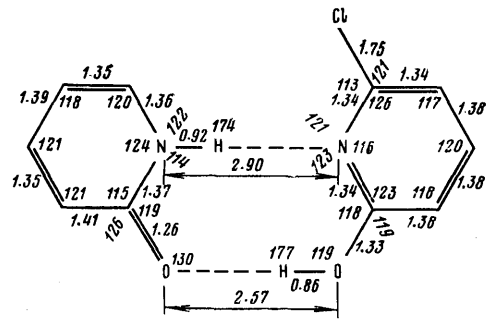


Figure 9.

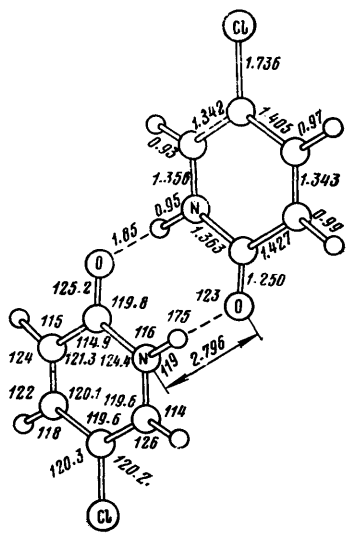


Figure 10.

A significant substituent influence on the stabilisation of a particular tautomeric form has been observed also in 2-pyridone derivatives: 2-pyridone and its 6-chloro-derivative form a molecular complex in which the unsubstituted molecule is in the pyridone form, while the substituted molecule is in the hydroxypyridine form[30] (Fig.9). α-Pyridone itself[31], 5-chloro-2-pyridone[32], α-thiopyridone[33], and 3-hydroxy-6-methyl-2-thiopyridone[34] exist in the crystal

in the pyridone form, while 6-chloro- [35] and 6-bromo-2-hydroxypyridine[36] exist in the hydroxypyridine form. In all these structures the hydrogen bonds are intermolecular. The structural unit in both the pyridone and hydroxypyridine forms is in most cases a centrosymmetric dimer (Fig.10) and only in the α-pyridone crystal have infinite helical chains been found (Fig.11). Intramolecular hydrogen bonds are not formed in these systems, since the geometrical conditions (the closure of a three-membered ring) are very unfavourable for them.

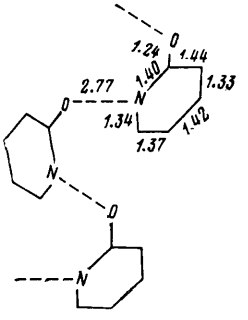
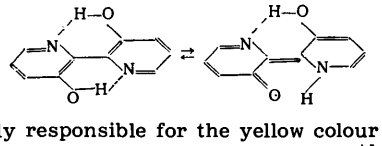


Figure 11.

However, when a hydrogen atom is replaced by a tin atom, a chelate structure becomes possible. Dichlorobis(2-pyridinethiolato)tin has such a structure[37]. In contrast to triphenyltin pyridine-4-thiolate[20] (see above), the Sn–S bonds in these molecules (with an average length of 2.464 Å) are slightly lengthened compared with the normal single bond; at the same time the Sn–N bond length (2.264 Å) also exceed the sum of the covalent radii only by 0.16 Å. This behaviour can be explained by the enhancement of the coordinating capacity of the metal atom and the enhancement of the electron-accepting properties of the substituents, which has been frequently quoted in the literature (see, for example, Furmanova et al.[38]). The distribution of bond lengths in the nucleus is intermediate between those for the mercaptopyridine and thiopyridone forms: the C–S bond lengths are 1.74 Å, the average lengths of the formally double C=C bond in the ring (for the *o*-quinonoid structure) are 1.37 Å, and the lengths of single bonds are 1.41 Å.

In hexakis(2-pyridone)copper perchlorate[39] the complex includes pyridone molecules which have retained the H atoms of their NH groups (the positions of these atoms have been determined objectively by X-ray diffraction) and accordingly exist in a distinctly pyridone form (Fig.12). A somewhat different quinonoid form contributes to the structure of 2,2′-bis-6-methyl-3-pyridinol[40] (Fig.13):



It is apparently responsible for the yellow colour of the compound. In the crystals of 2-aminopyridine[41] and 2-amino-5-chloropyridine [according to the data of Kvick and Backens[42] (X-ray diffraction) and Kvick et al.[43] (neutron diffraction)], as well as in the structures of 2-hydroxypyridine derivatives the molecules form centrosymmetric dimers via N–H...N hydrogen bonds with lengths of 3.071 and 3.058 Å. The C–NH_2 bonds in both molecules [1.351(2) and 1.357(2) Å] are shorter than in the 3-aminopyridine molecule [(1.384(4) Å] incapable of giving rise to the quinonoid form[44].

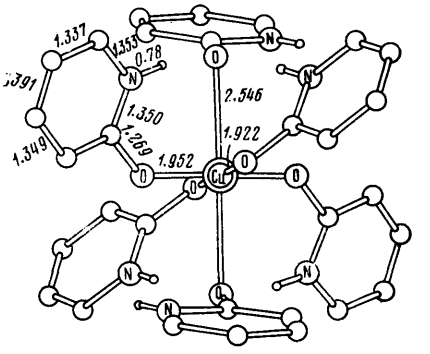


Figure 12.

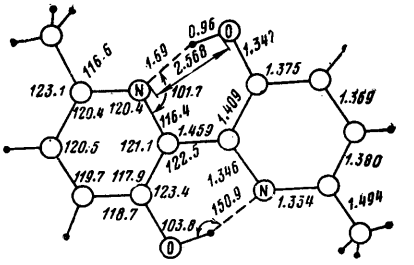


Figure 13.

IV. QUINONE OXIMES AND AMINOQUINONES

An equalised structure, which precludes a conclusion about the predominance of a particular form, obtains in the crystal of triphenyl-lead 2-fluoro-4-nitrosophenoxide[45]. The crystal is made up of infinite chains (Fig.14). The Pb atom has a trigonal-bipyramidal coordination with the O atoms in the axial positions. The difference between the Pb–O bond lengths (2.43 and 2.50 Å) is close to the error in their determination. Three Pb–C bonds are coplanar: the sum of the C–Pb–C angles is 359.9° and the average O(1)–Pb–C and O(2′)–Pb–C angles are 89.8° and 90.4°. Thus, neither the Pb–O distances nor the valence angles at the Pb atom indicate the predominance of a particular form and the structure is best described as a resonance hybrid with equal contributions by the quinone oxime and nitrosophenol forms.

Infinite chains formed via hydrogen bonds have also been found in the structure of free *p*-quinone oxime[46], but the molecule of this compound exists in the crystal as a distinct quinone oxime form (Fig.15). On the other hand, the C=N bond (1.309 Å) is longer and the N–O bond (1.374 Å) is shorter than in cyclohexane-1,4-dione dioxime (1.276 and

1.411 Å respectively[47]), although the H atom of the oxime groups of the latter molecule are also involved in the formation of hydrogen bonds. Thus a partial redistribution of the π-bonds is manifested distinctly only for the *p*-quinone oxime system capable of a tautomeric transformation.

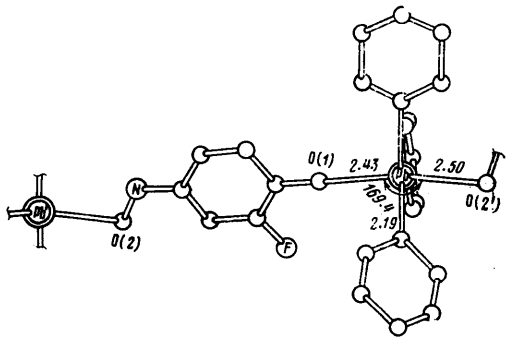


Figure 14.

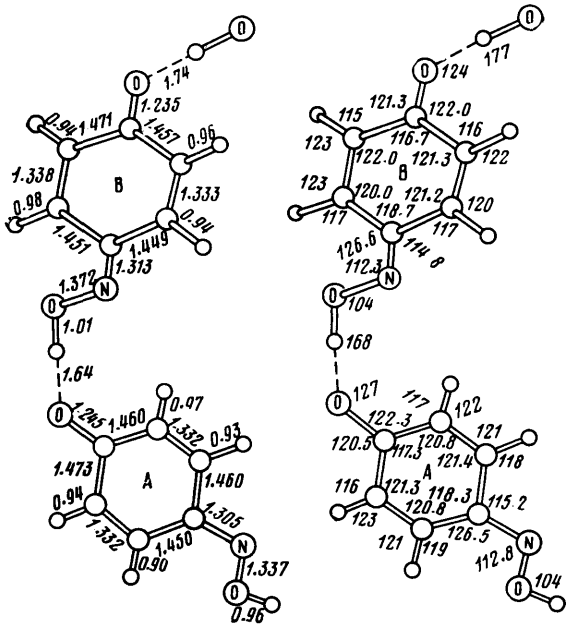


Figure 15.

6-Chloro-3-methyl-*p*-nitrosophenol, 6-bromo-3-methyl-*p*-nitrosophenol, and 3-chloro-*p*-nitrosophenol, investigated previously on the basis of projections, have similar structures[48,49]. It would be of interest to compare the structures of these compounds with those of their analogues incapable of association in the crystal. Unfortunately, although such structures are known—the acetates of *syn*- and *anti*-2-bromo-*p*-benzoquinone oximes and 2-chloro-*p*-benzoquinone oxime[50,51]—the low accuracy of their determination precludes a detailed analysis of the geometrical parameters of the molecules (such a comparison has been carried out for amino-derivatives of β-naphthoquinones—see below).

An oxime structure with a small contribution of the nitroso-form is also characteristic of *syn*- and *anti*-pyridine-4-carboxaldehyde oximes[52,53] and *syn*- and *anti*-pyrimidine-4-carboxaldehyde oximes[54,55]. As in the structures of *p*-benzoquinone oximes, in the crystal the molecules of these compounds form infinite chains via hydrogen bonds.

o-Quinone oximes were investigated approximately 20 years ago and the accuracy of these studies is unfortunately not very high. These compounds crystallise in two forms—orange and green. On the basis of spectroscopic and crystal-optical data, it was suggested that the more stable orange α-form corresponds to the quinone oxime structure and the green β-form corresponds to the nitrosophenol structure. The structure of the orange form was determined (on the basis of projections) for 5-methoxy-*o*-quinone 2-oxime[56]. Its molecules do indeed exist in the *anti*-configuration of the quinone oxime form and are linked into infinite chains via hydrogen bonds (Fig.16); the consideration of specific geometrical parameters would not be justified in view of the accuracy obtained. The structure of the green β-form of 5-n-propoxy-*o*-quinone 2-oxime has been determined[57] and it was found that in this case the quinone oxime form predominates (Fig.17), although the molecule has the *syn*-configuration with a strong intramolecular hydrogen bond. The nature of the absorption spectrum, which does not correspond to the oxime structure, can apparently be accounted for by the presence of this bond and a significant contribution of the nitrosophenol form.

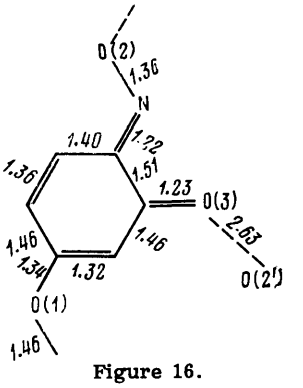


Figure 16.

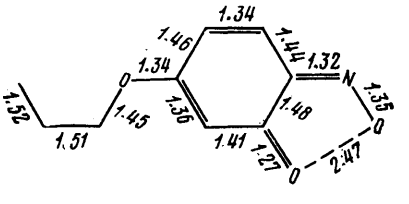


Figure 17.

The crystals of potassium *p*-nitrosophenoxide monohydrate (green)[58], magnesium *p*-nitrosophenoxide hexahydrate (reddish green)[59], and sodium *p*-nitrosophenoxide trihydrate (pale red)[60] also have different colours.

Unfortunately the accuracy of the determination of the structure of the potassium salt is insufficient for the analysis of the electronic structure of the anion. On the other hand, comparison of the geometrical parameters of the *p*-nitrosophenoxide anion in the sodium (Fig.18*a*) and magnesium (Fig.18*b*) salts showed that, as in *o*-quinone oximes, the green colour is associated with a large contribution of the nitrosophenol form, although the latter does not predominate. Comparison of these three structures also shows how much the electronic structure of the *p*-nitrosophenoxide anion depends on the nature of the cation and the system of hydrogen bonds in the crystal.

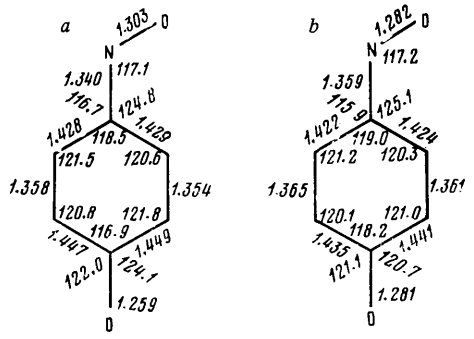


Figure 18.

In all the structures examined in this section (with the possible exception of that of triphenyl-lead 2-fluoro-4-nitrosophenoxide) the quinone oxime form predominates. The nitrosophenol structure has been found only in the molecule of 5-nitrososalicylic acid[61], where the H atom of the hydroxy-group is involved in a strong hydrogen bond with the carboxy-group, as in salicylic acid itself (Fig.19).

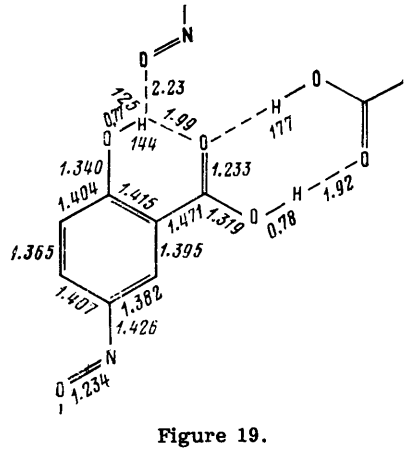


Figure 19.

1,2-Naphthoquinone 1-oxime[62] and its 6-t-butyl derivative[63] have the quinone oxime structure and the *syn*-configuration with an intramolecular hydrogen bond. On the other hand, in the metal (Ni, Cu, Hg) complexes of 1,2-naphthoquinone oximes a five-membered ring is formed in which the NO group coordinates the metal atom via the N and not the O atom, rather than a six-membered chelate ring; the ligand has the *anti*-configuration[64-67]. The copper, nickel, and zinc complexes with 1,2-naphthoquinone oxime ligands containing sulpho-groups in the 4- or 5-position have analogous structures[68-70]. The sulpho-derivatives of 1,2-naphthoquinone oximes themselves (with the sulpho-groups in the 5-, 7-, or 8-position) have the *anti*-configuration, in contrast to their analogues without sulpho-groups[71-75]; the H atom of the oxime group in these structures forms an intermolecular hydrogen bond with an O atom of the sulpho-group. The molecule of 7-hydroxyimino-8-oxoquinoline-5-sulphonic acid in the crystal[76] and its anion in the structure of the disodium salt[76] also exist in the *anti*-configuration.

It is noteworthy that in the naphthoquinone oxime molecules examined above, in both the *syn*- and *anti*-configurations, the quinone oxime tautomeric form is very pronounced: the bond lengths vary in the ranges 1.20 to 1.25 Å for C–O, 1.30–1.31 Å for C–N, 1.35–1.39 Å for N–O, and 1.47–1.52 Å for C–C (between the carbonyl and oxime groups). In the quinone oximate anion[76] the contribution of the nitroso-form is somewhat greater: the bond lengths (1.28 Å for C–O, 1.35 Å for C–N, 1.28 Å for N–O, and 1.44 Å for C–C) are close to those found in sodium *p*-nitrosophenoxide[60] (see above). The quinone oximato-ligand has similar geometrical parameters also in the metal complexes.

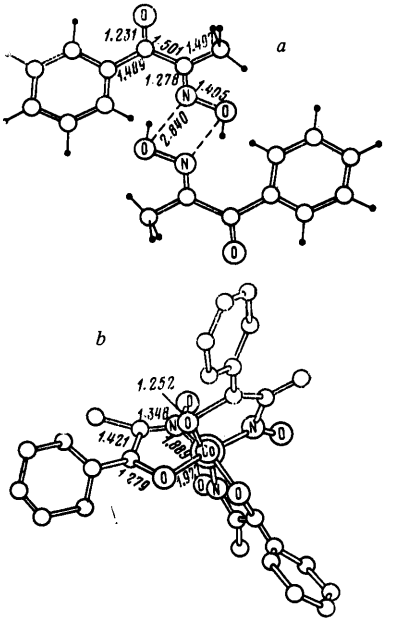
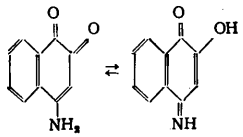


Figure 20.

The oxime form is very distinct also in the structure of 1-phenylpropane-1,2-dione 2-oxime[77] (Fig.20*a*), where the molecules are combined into centrosymmetric dimers via O–H...N hydrogen bonds, while in the cobalt complex[78] this ligand assumes an intermediate structure, like the naphthoquinone oximato-ligand (Fig.20*b*).

The example of naphthoquinone oximes shows that, although the structures with a hydrogen bond between two nucleophilic centres of potentially tautomeric systems are the main ones, they are not the only ones possible for such crystals: when the molecule contains other nucleophilic centres, for example, the sulpho-group, the *a priori* prediction of the structure requires estimates of the energies of the different variants of the resultant structure.

It must also be emphasised that the delocalisation of π-electrons, which is so characteristic of potentially tautomeric systems with hydrogen or secondary (coordinate) bonds, can be observed also in structures where such bonds are absent. The structures of 4-amino-1,2-naphthoquinones[79], where tautomerism is possible in principle, may serve as a good illustration:



The structures of 4-amino-3-bromo-1,2-naphthoquinone, its monohydrate, and methanol solvate, as well as the structures of the monohydrate of 4-amino-3-methyl-1,2-naphthoquinone, 4-diethylamino-1,2-naphthoquinone, and 4-dimethylamino-1,2-naphthoquinone have been determined[79]. In the first four structures there are intermolecular N–H...O hydrogen bonds between the NH_2 group and the CO group in the β-position. The average bond lengths in the N–C=C–C=O chain in these molecules are 1.322, 1.392, 1.405, and 1.246 Å. In the last two structures there are no hydrogen bonds, but the π-bonds are nevertheless delocalised, reflecting the significant contribution of the dipolar form $H_2\overset{+}{N}=C-C=C-\bar{O}$; however, the average bond lengths (1.358, 1.376, 1.418, and 1.237 Å) show that the delocalisation is appreciably weakened in the absence of hydrogen bonds.

V. FORMAMIDINES AND TRIAZENES

If the tautomeric rearrangement is degenerate, then X-ray diffraction makes it possible to distinguish a rapid exchange process from the symmetrical structure equalised as a result of chelate formation in those cases where the NMR method cannot provide an unambiguous answer to this question. An example of such a structure is *N*-phenylmercuri-*N*,*N'*-ditolylformamidine[80]. In the ^1H, ^{19}F, and ^{13}C NMR spectra of this and related compounds the signals of the indicator groups in the *p*-positions of the aromatic rings consist of singlets and the protons of the rings themselves give rise to a symmetrical quartet A_2B_2.

The structures of two crystallographically independent molecules, found by X-ray diffraction, are illustrated in Fig.21. The bond between the phenylmercuri-residue and the formamidine fragment is different in them: in the A molecule the Hg atom forms a normal covalent bond with the N(1) atom, having a length of 2.13(3) Å. The Hg...N(2) distance (2.68 Å) is shortened compared with the sum of the van der Waals radii by ~0.5 Å and indicates the occurrence of coordination interaction. In the B molecule the Hg'...N(2') distance (3.19 Å) is significantly greater than in the A molecule and is virtually equal to the sum of the van der Waals radii, i.e. in the B molecule the coordination interaction is either absent or very weak. At the same time, there is a weak intermolecular interaction between neighbouring type B molecules [the Hg'...N(2'') distance is 3.08 Å]. Thus the characteristics of the spectra of the *N*-phenylmercuri-derivatives of *N*,*N'*-diarylformamidines are due to the rapid reversible intramolecular exchange of the phenylmercuri-residue between the N atoms of the amidine triad. Such exchange is facilitated by the intramolecular coordination observed in the A molecule.

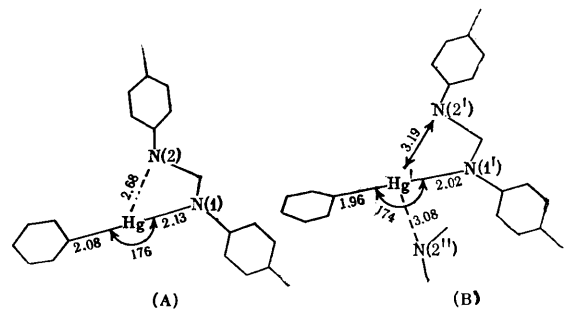


Figure 21.

In the molecule of the phenylmercuri-derivative of 2-chlorodiazoaminobenzene[81] the Hg atom forms a covalent bond with one N atom of the triazene system (Hg–N = 2.14 Å) and is coordinated to the other atom (Hg...N = 2.46 Å). The geometries of the triazene and formamidine systems are not very favourable for the formation of a secondary Hg...N bond, because the N–Hg...N angle is much smaller than the ideal value for the Hg atom (90°). Systems of this type are even more unfavourable for the formation of an intramolecular hydrogen bond.

Indeed the binding of the molecules into helical chains by N–H...N intermolecular hydrogen bonds is characteristic of the diazoaminobenzene structures. The crystals of the α- and β-modifications of diazoaminobenzene[82,83], the β-modification of *p*-bromodiazoaminobenzene[84,85], the *p*-methyl- and *p*-chlorodiazoaminobenzenes[86], and *p*,*p'*-dimethyl, *p*,*p'*-dichloro-, and *p*,*p'*-dibromodiazoaminobenzenes[87,88] are constructed in this way. Cyclic dimers are formed via N–H...N hydrogen bonds only in the α-modification of the *p*-bromodiazoaminobenzene molecule[85]. In two structures—those of *p*-nitrodiazoaminobenzene[89] and 2,4-dibromodiazoaminobenzene[90]—the N–H...N hydrogen atoms are absent. The packing of the molecules in the former structure is determined by the N–H...O hydrogen bonds with the nitro-group; a short N...Br contact has been found in the latter molecule, which may also correspond to a hydrogen bond.

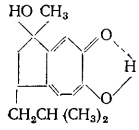
Unfortunately the accuracy of the results of all these studies is low and precludes a conclusion concerning the distribution of hydrogen atoms and bond lengths in the triazene chain.

VI. TROPOLONES

Structures with chelate rings are known for mercury (but not in its organic derivatives). Mercury tropolonate, for example, has such a structure[91]: both tropolonate ligands form chelate rings with Hg–O distances of 2.30 Å; the planes of the two ligands form an angle of 85° relative to one another. Tropolone forms symmetrical chelate complexes, similar to the mercury complex described by Allman et al.[91],

also with other metals, for example iron[92], zirconium[93], and copper[94].

Tropolone itself is a tautomeric system[95] and the independence of the signal of the hydroxyl proton in the ^{1}H NMR spectrum of concentration indicates an intramolecular process mechanism[95,96]. However, the geometry of the tropolone molecule is not optimal for the formation of a chelate ring via an intramolecular hydrogen bond and in the crystal tropolone molecules form dimers with a forked hydrogen bond incorporating both intramolecular and intermolecular components[97] (Fig.22). Dimers with a similar structure have also been discovered in the crystals of 4-isopropyltropolone[98,99], 5-isopropyltropolone[100], 3,7-dibromo-6-isopropyltropolone[100], and 5,7-dibromo-4-isopropyltropolone[101]. According to electron diffraction data[102], in the gas phase an asymmetric hydrogen bond is formed in the tropolone molecule. An intramolecular hydrogen bond is apparently also formed in 3,5,7-tribromo-6-isopropyltropolone[103] and chanootin[104]:



In the crystal of ditropolonylfuran[105] dimers having a forked hydrogen bond are formed with participation of one tropolone ring, while in the other ring only an intramolecular hydrogen bond is produced.

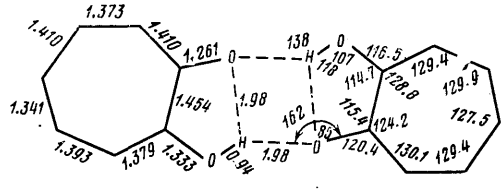


Figure 22.

Carbonotropic systems have been recently synthesised in the series of tropolone derivatives[106,107] (Fig.23). It has been shown by dynamic NMR that the activation barrier to the rearrangement A ⇌ B in solution amounts to 26 kcal mol^{-1} for the *p*-nitrophenyl ether (I). On passing to the 2,4-dinitrophenyl ether (II), it decreases to 11.7 kcal mol^{-1} and for the 2,6-dinitrophenyl ether (III) it becomes so low that, in terms of the ^{1}H NMR time scale, the molecule has an effective C_{2v} symmetry, i.e. a type (B) structure, although the electronic absorption spectra of solutions indicate an asymmetric molecular structure; the 2,4,6-trinitrophenyl derivative has a true symmetrical structure (BIV), i.e. is the first example of a zwitter-ionic Meisenheimer σ-spiro-complex. The (BIV) structure has been confirmed by X-ray diffraction[108]. The molecule in the crystal is located on a two-fold axis (Fig.24). The plane of the cyclohexadienyl ring is almost perpendicular to the remaining portion of the molecule, the angle between them amounting to 85.8°. The C(4) atom is tetrahedral, the angles at the latter varying in the range 101.9–112.4°. The bond lengths in the seven-membered ring are equalised (1.379–1.401 Å), which is characteristic of the tropylium cation. In the six-membered ring the C(3)–C(4) bond length is 1.486 Å, which is appreciably greater than the aromatic bond lengths (1.394 Å) and approaches the length of a single C(sp^2)–C(sp^3) bond (1.510 Å).[28] The lengths of the remaining C–C and C–N bonds indicate the delocalisation of the negative charge over the ring and the nitro-groups.

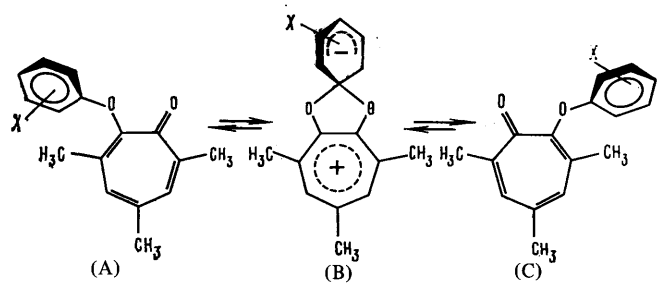


Figure 23.

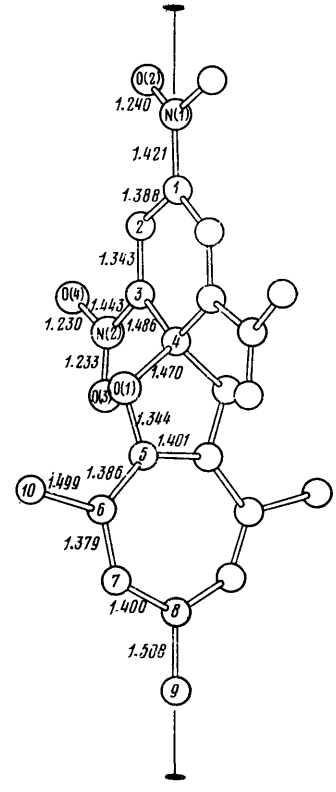


Figure 24.

X-Ray diffraction analysis of the (AIII) structure yielded particularly interesting results[108]. Despite the possibility of rotation about the O(1)–C(7) and O(1)–C(1) bonds (Fig.25), the molecule assumes a conformation in which the C(1) atom approaches to the maximum possible extent

the O(2) atom and the C(1)...O(2) distance, which is 2.451 Å, is significantly shorter than the sum of the van der Waals radii (~3.2 Å).[21] As in the (BIV) structure, the plane of the six-membered ring is almost perpendicular to that of the tropolone system (the angle between them is 84.9°), i.e. the conformation of the (AIII) molecule is optimal for the closure of a five-membered ring with formation of a spiro-structure of type (BIV). Furthermore, the C(1) atom is displaced by 0.09 Å from the plane of the three atoms linked to it, in the direction of the O(2) atom, while the C(1)...O(2) line is approximately perpendicular to the O(1)C(1)C(2)C(3) fragment. All these geometrical features show that a configuration fairly close to the structure of the transition state in the first stage (A ⇌ B) of the intramolecular rearrangement A ⇌ C obtains in the (AIII) structure. These geometrical features actually explain the exceptionally high frequency of the migration of the 2,6-dinitrophenyl group in (AIII) solutions.

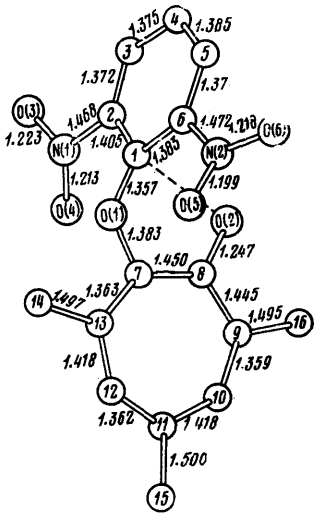
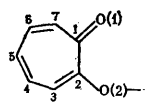


Figure 25.

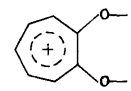
The observed molecular conformation is possible only in the presence of a strong C(1)...O(2) interaction. In the absence of such interaction, the molecule assumes a transoid configuration relative to the C–O bond, as, for example, in *p*-chlorobenzoyltropolone[109]. It is noteworthy that the energy barriers to the *O,O'*-aroyl migrations in tropolone derivatives are much higher than the barriers to the migrations of the 2,6-dinitrophenyl group[106] and there is thus a direct relation between the structure of the molecule and its dynamic behaviour. At the same time it must be emphasised that the occurrence of an intermediate state with a strong intramolecular C(1)...O(2) interaction in the (AIII) crystal proved to be possible as a result of a particularly favourable geometry of this system[107].

Comparison of data for tropolone derivatives makes it possible to distinguish three limiting types of their electronic structure. Type I is a structure with localised double bonds:



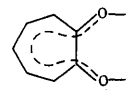
The structure of *p*-chlorobenzoyltropolone[109] with the bond lengths C=O = 1.225, C–O = 1.388, and C(1)–C(2) = 1.459 Å, while the average values of the remaining bonds are C–C = 1.419 Å and C=C = 1.338 Å, is closest to this type.

Type II is the structure of the tropylium cation (a six-electron π-system) with delocalisation of the π-electrons over the ring:



A type II structure obtains in tropolone hydrochloride[110] (with the bond lengths C–O = 1.365 and C–C = 1.38–1.41 Å) and the 2,4,6-trinitrophenyl ether of tropolone[108] (C–O = 1.344 Å and C–C = 1.379–1.401 Å).

Finally type III is a structure with a delocalised π-electron system not including the C(1)–C(2) bond but including the C–O bond (a ten-electron π-system):



Sodium tropolonate[111,112] (C–O = 1.278 Å, C(1)–C(2) = 1.478 and with the remaining C–C bond lengths of 1.388–1.426 Å) and the metal complexes mentioned above have this structure. This form makes some contribution to the structures of numerous hydrogen-bonded tropolone derivatives, which is manifested primarily by a lengthening of the C=O bond (~1.25–1.26 Å) and a shortening of the C–O bond (~1.33–1.35 Å); the C(1)–C(2) bond length is 1.45–1.50 Å, the remaining C–C bond lengths in the ring are 1.40–1.44 Å, and the C=C bond lengths are 1.35 to 1.37 Å.

The considerable delocalisation of the π-electrons in these systems, as in the systems discussed previously, is due precisely to the formation of a hydrogen bond. SCF–MO calculation[113] without allowance for this bond leads to a more delocalised system [C=O = 1.258 Å, C–O = 1.389 Å, C–C = 1.452–1.462 Å, and C=C = 1.355–1.357 Å; the C(1)–C(2) bond length does not differ from that of the other C–C bonds in the ring].

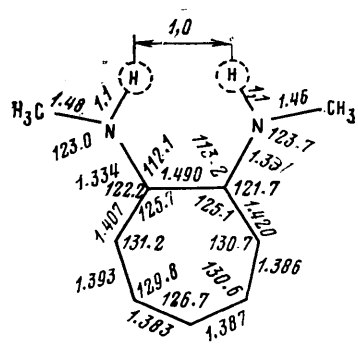


Figure 26.

In contrast to these derivatives, the nitrogen analogue of tropolone—1-methylamino-7-methyliminocyclohepta-1,3,5-triene—has a type III structure in an almost pure form[114]. According to X-ray diffraction data (Fig.26), a hydrogen

atom in the molecule is distributed between two equivalent positions at a distance of ~1.0 Å from one another and at a distance of ~1.1 Å from the nearest N atom. A detailed analysis of thermal vibrations showed that this structure is not a result of a disordered statistical superposition of two "tautomers" but corresponds to a symmetrical system with a very low energy barrier to the transition of the H atom from one potential well to another. This description is consistent with infrared spectra[115] and with ^{1}H NMR spectra[114], in which the protons of the CH_3 groups give rise to a singlet signal even at −80 °C.

VII. β-DIKETONES

β-Diketones also form symmetrical chelate rings with the bond lengths C−C ≅ 1.39 Å and C−O ≅ 1.27 Å in complexes with most metals (see, for example, Lingafelter and Braun[8]). The acetylacetonate anion in the potassium salt also has a structure with delocalised bonds[116]. However, β-diketones can also give rise to a C-form with an Hg atom, which has not been found for tropolonate complexes.

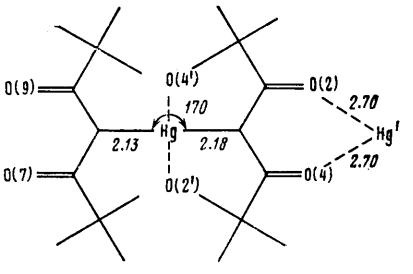
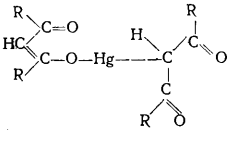


Figure 27.

Mercury bispivaloylmethanate has such a structure in the crystalline state[117,118] (Fig. 27). The Hg atom in this molecule forms somewhat lengthened Hg−C bonds (2.13 and 2.18 Å) with the two dipivaloylmethanate groups (the normal Hg−C bond length is 2.07−2.11 Å) and weak coordinate bonds having a length of 2.70 Å with the two oxygen atoms of a neighbouring dipivaloylmethanate group (the length of the covalent Hg−O bond is 2.03−2.07 Å. The ^{1}H NMR spectra showed that in solution in chloroform the molecules of this compound are monomeric, but a weak signal at 5.75 p.p.m. indicates the presence of ~5% of the enolic form together with the initial diketo-form. According to Fish[119], the content of the enolic form in solution in ethanol rises to 50% and the molecular structure is described by the formula



The molecules of (nonane-4,6-dionyl)trimethylplatinum are dimeric both in the crystal and in solution[118]. In this dimer (Fig. 28) the Pt−O bonds (2.14 and 2.16 Å) (the normal value is 1.97 Å) may be regarded as the main ones, while the Pt−C bond (2.39 Å) is "additional" (the normal length of the Pt−C σ-bond is 2.02 Å), i.e. the bonds are more equalised in this structure.

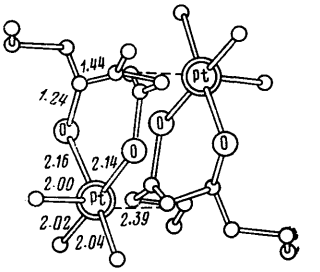


Figure 28.

According to X-ray diffraction studies, the non-coordinated β-diketone molecules exist in the enolic form and have a cisoid conformation with a very strong intramolecular hydrogen bond. Depending on the nature of the substituents, both an almost symmetrical structure with approximately equalised bonds, for example, in benzoylacetone according to X-ray diffraction data[120] and neutron diffraction data[121], and a highly asymmetric structure with a distinct predominance of one of two enolic forms, for example, in 1-(2-thienyl)-4,4,4-trifluorobutane-1,3-dione[122] (Figs. 29*a* and 29*b*), can obtain.

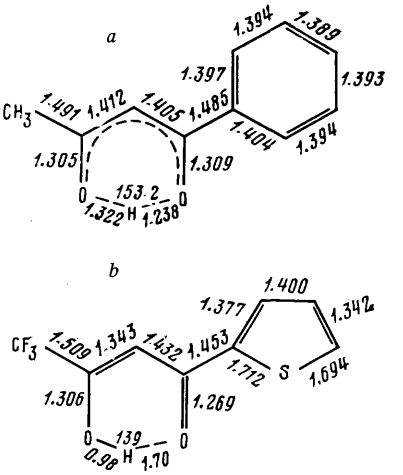


Figure 29.

The structure of the last compound agrees with the results of a calculation by the CNDO/2 method[123], which showed that the proton should be localised at the carbonyl group with the more electronegative β-substituent. However, a fully equalised structure with a highly symmetrical hydrogen bond has not been found among β-diketones. In all the structures

where the position of the hydrogen atom has been determined fairly reliably from X-ray or neutron diffraction data (see, for example, Refs.124–129), the atom is displaced towards one of the oxygen atoms and this displacement is correlated with the difference between the C–C and C–O bond lengths. It is noteworthy that there is no fundamental difference between symmetrical and slightly asymmetric hydrogen bonds[130]. The adiabatic potential of a hydrogen atom involved in very strong hydrogen bonds has a broad and shallow minimum and even the very weak perturbations due to the asymmetry of the environment of the molecule in the crystal are sufficient to infringe the symmetry of this bond[131].

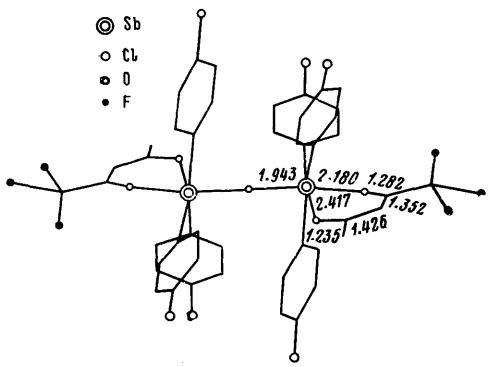


Figure 30.

A strong intramolecular O–H...S bond is formed in 3-mercapto-1,3-diphenylprop-2-en-1-ol [132] (according to neutron diffraction data, the bond lengths are O–H = 1.024 Å, H...S = 1.904 Å, and O...S = 2.865 Å), i.e. the compound exists in the crystal in the enolic (and not the thioenolic) form; the C–O bond (1.321 Å) is comparatively long, while the length of the C–S bond (1.675 Å) is close to that of a double bond. The chelate ring in μ-oxobis[tris(*p*-chlorophenyl)(1,1,1-trifluoropentane-2,4-dionato)antimony] has a highly asymmetric structure[133] (Fig.30), while in the octahedral acetylacetonate complexes [(acac)CH_3SbCl_3], [(acac)$(CH_3)_2SbBr_2$], and [(acac)Ph_2SbCl_2] [134] the chelate rings are symmetrical. In (1,3-diphenylpropene-1,3-dionato)triphenyltin[135], with a trigonal-bipyramidal coordination of the metal atom, the equatorial Sn–O(1) bond (2.094 Å) is shorter than the axial Sn–O(2) bond (2.276 Å). Accordingly the bonds in the diketonate ligand are also non-equivalent: the lengths of the bonds closest to O(1) are C–O = 1.29 Å and C–C = 1.36 Å, while those of the bonds closest to O(2) are C–O = 1.26 Å and C–C = 1.40 Å.

Phosphonia-β-diketones have a somewhat different structure. The α-triphenylphosphoniabenzoylacetone cations also exist in the enolic form in the crystal but have the *trans*-configuration, forming a hydrogen bond with Cl^- (Fig.31) or BF_4^- ions[136,137]. The chloride of α-triphenylphosphoniaacetoacetic ester has a similar structure[138]. In contrast to the *cis*-enols, in the *trans*-enols the planarity of the enolic system is appreciably infringed and the bond lengths are closer to the standard values: C–C = 1.49–1.56 Å, C=C = 1.31–1.37 Å, C–O = 1.32–1.33 Å, and C=O = 1.17–1.24 Å.

Acetylacetone has been investigated by electron diffraction in the gas phase and it has been observed that at the experimental temperature (~105 °C) the content of the enolic form in the gas is 66%.[139] The geometrical parameters of the enolic and diketo-forms are presented in Fig.32. At room temperature the equilibrium is displaced towards the symmetrical enolic form according to electron diffraction data[140]. The electron diffraction data for trifluoroacetylacetone[140] and hexafluoroacetylacetone[141] also agree best with the symmetrical enolic structure.

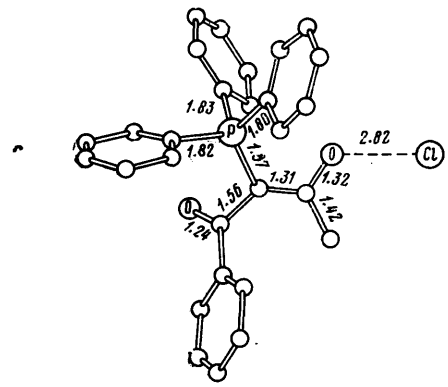


Figure 31.

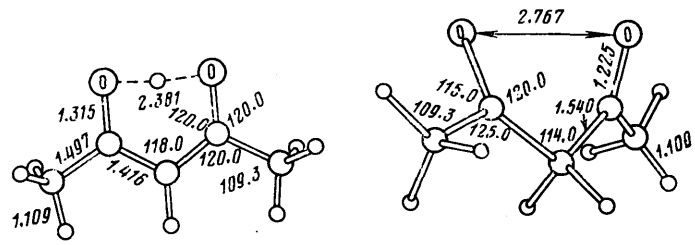


Figure 32.

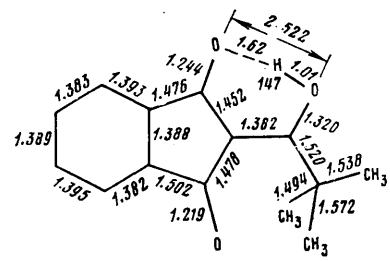


Figure 33.

In the 2-pivaloylindan-1,3-dione molecule[142] one of the carbonyl groups is involved in a keto–enol system with a strong intramolecular hydrogen bond, while the other remains free (Fig.33). This structure makes it possible to observe particularly distinctly the lengthening of the C=O bond in the chelate ring and the shortening of the C–C bond in

the latter, in conformity with the partial contribution of the second tautomeric form to the structure.

In the series of acetylacetone derivatives, as in the tropolone series, carbonotropic tautomerism has also been observed[107], but there are virtually no X-ray diffraction data for compounds of this class. X-Ray diffraction analysis of the picryl derivative of acetylacetone *N,N'*-dimethyldiimine[143], on the basis of which the intramolecular migration of the picryl group between the two N atoms might have been postulated (Fig.34), showed that this compound is a *C*-derivative (formula C).

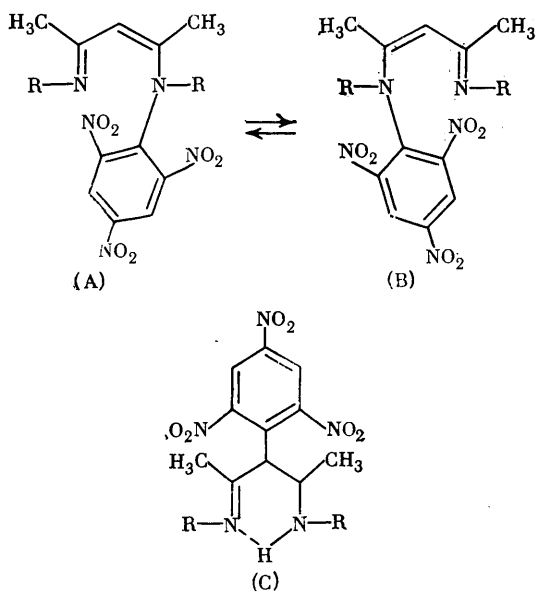


Figure 34.

VIII. MOLECULAR GEOMETRY AND INTRAMOLECULAR REARRANGEMENTS

Thus the formation of hydrogen (in the case of prototropism) or secondary (in the case of metallo- and carbono-tropism) bonds is characteristic of all tautomeric and potentially tautomeric systems. The relation between the geometries of the molecules and their capacity for intramolecular rearrangements has been traced for some of the examples described above.

The relation between the geometry of the molecule and its ability to undergo the *trans*-acylation reaction has been noted in X-ray diffraction studies on naphthazarine[144] (Fig.35) and tetramethylnaphthazarine[145] diacetates. In these molecules the planes of the acetyl groups are almost perpendicular to the plane of the naphthazarine ring, but are nevertheless somewhat inclined towards the quinonoid oxygen atom, which shortens the C...O distances to 2.68–2.75 Å, although, at least for the first molecule, there is a possibility of the deviation of this group in the opposite direction. Thus even in the ground states of these molecules there exists a basis for the transfer of the acyl group to the neighbouring O atom. However the C...O interaction in these systems is weak and does not distort the C=O and C–O bond lengths.

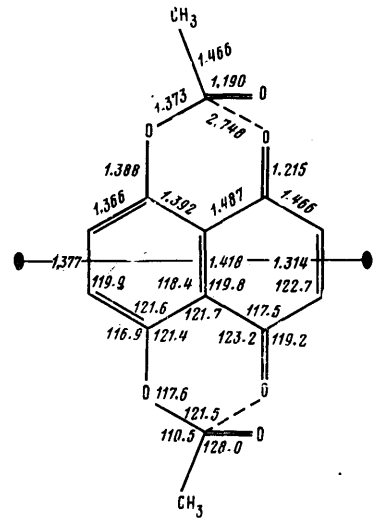
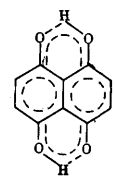
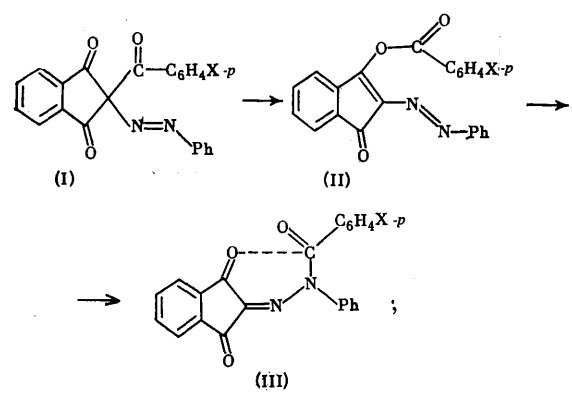


Figure 35.



In naphthazarine itself there is a strong slightly asymmetric O–H...O hydrogen bond, so that the structure is nearly mesomeric, but with a slight predominant contribution of the 4,8-dihydroxy-1,5-naphthoquinone form[146]. Shortened intramolecular C...O distances between the carbon atom of the benzoyl group and the oxygen atom of the carbonyl group (2.673, 2.638, and 2.835 Å) have also been found in the structures of the 2-(*N*-benzoyl-*N*-phenylhydrazones) of indan-1,2,3-trione (III),[147,148] which are formed instead of the expected enol benzoates (II) on thermal rearrangement of the corresponding azo-compounds (I):



X = H (*a*), Br (*b*), or t-Bu (*c*).

In the crystal these molecules can exist both in the *syn*-configuration [compound (IIIa) and one of the independent molecules of compound (IIIb)] and in the *anti*-configuration [the second independent molecule of compound (IIIb) (?) and compound (IIIc)], the unusual stability of the sterically

strained *syn*-form being probably caused by the C...O interaction mentioned above. This interaction creates almost ideal conditions for the rearrangement (III) ⇌ (II), which apparently makes the (II) → (III) transition very rapid during the reaction and precludes the observation of the intermediate formation of (II). One should note that the C...O interaction observed in these structures is fairly weak and does not alter appreciably the bond lengths in the *syn*-form compared with the *anti*-form.

IX. FULVENES

The derivatives of pentafulvenes are also interesting keto-enol systems. 6-Hydroxyfulvene-1-carboxaldehyde has been investigated by X-ray and neutron diffraction[149]; two of its nitro-derivatives—2,3-diacetyl- and 2,3-dibenzoyl-5-nitrocyclopentadiene—have also been subjected to X-ray diffraction analysis[150]. The diketo-form (I) (Fig.36), a tautomeric equilibrium between the enolic fulvene forms (II) (which appears most probable on the basis of spectroscopic data), or a delocalised symmetrical structure (IV) are possible in principle for these compounds. The ^{1}H NMR data for the nitro-derivative also do not conflict with structure (III). Studies[149,150] have shown that in the crystals of all three compounds structure (IV) is formed.

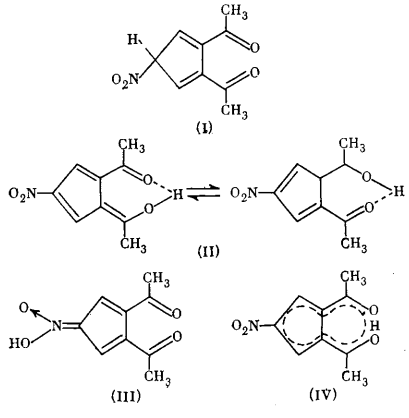


Figure 36.

The enolic hydrogen atom is located at approximately equal distances from both oxygen atoms (although in an X-ray diffraction study of 6-hydroxyfulvene-1-carboxaldehyde the hydrogen atom gave rise to a double electron density peak, but in the remaining cases the location of this atom was unambiguous) and the molecular symmetry is close to C_{2v}. The length of the central C–C bond is 1.462–1.467 Å, which is close to that of a single bond in cyclo-octatetraene (1.462 Å), while the lengths of the remaining C–C and C–O bonds are close to values correspondng to a bond order of 1.5, i.e. the delocalisation involves mainly the outer ring and affects the central bond to only a slight extent. Quantum-chemical calculations have led to an analogous conclusion[150].

In the crystal of the nitrogen analogue—*N*,*N*'-diphenyl-6-aminopentafulvene-2-aldimine[151]—the hydrogen atom is distributed between two positions (Fig.37), which can be a result of either a statistical superposition of two asymmetric forms, which can undergo tautomeric transitions only in solution, or of the migration of the hydrogen atom between two equilibrium positions also in the crystal. Analysis of thermal vibrations suggests that preference should be given to the last variant.

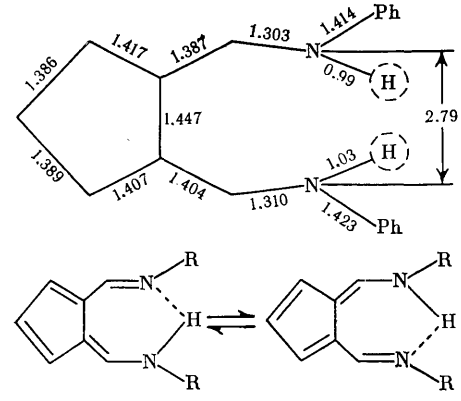


Figure 37.

* *
*

Thus the data examined have shown that in all cases of potentially tautomeric systems without exception a coordination interaction has been observed (a hydrogen bond in prototropic systems), resulting in a greater or smaller contribution of both possible tautomeric forms to the structure and ultimately in a resonance hybrid with equal contributions of both forms. The occurrence of hybrid forms in the crystal implies that their formation in the tautomeric transition requires a minimal energy expenditure. One can therefore assume that in systems where there is a possibility of intramolecular coordination, the tautomeric transformation in solution also proceeds via the formation of hybrid forms with this type of coordination.

One can also assume that in systems with highly asymmetric secondary (hydrogen) bonds, the tautomeric transition takes place more readily the stronger this bond. On the other hand, if a structure close to a resonance hybrid of two tautomeric forms obtains in the crystal, it is most likely to be stable also in solution, i.e. the system is not tautomeric. The latter is valid, for example, for the Meisenheimer tropolone spiro-complex discussed in this review. In order to confirm the general nature of the relations indicated and to obtain quantitative estimates, joint systematic studies on the geometry and tautomeric behaviour of the molecules, which are virtually completely lacking at the present time (particularly for metallotropic compounds), are necessary.

For systems with intermolecular coordination, the appearance of a hybrid transition state requires the formation of associated species, apparently with a cyclic structure, and kinetic studies are necessary for the solution of the problem of the mechanism of the transition. There is as yet no direct confirmation of the mechanism of tautomeric transitions via associated molecular species but the characteristics of certain exchange reactions (the inverse dependence of the reaction rate on temperature, overall reaction order of ~4) can be accounted for precisely by the formation of associated

species. The exchange reaction between trimethyltin phenoxide and thiophenoxide can serve as an example[152].

The solution of this and many other problems of tautomeric transformations requires further joint structural and kinetic investigations.

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Sorption Mechanism of Metal Ions on the Salts of Heteropoly Acids

L.K.Neudachina and V.F.Barkovskii

Published data on the sorption properties of insoluble salts of heteropoly acids (HPA) are discussed in terms of recent views on the structure of HPA salts and on the tendency of ions to form heteropoly compounds, and a classification of ions which can be sorbed on HPA salts is proposed. The special features of the sorption mechanism of specific groups of ions are discussed, and sorption on HPA salts is shown to be a complex process, influenced by properties of the ions such as radius, ionic potential, state of the ion in solution, and tendency to form complexes. The sorption of ions which can form heteropoly compounds is a multi-step process, accompanied by interaction of the sorbed ions with the molybdophosphate anion. 111 references.

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I. INTRODUCTION

The ion-exchange properties of the salts of heteropoly acids (HPA) were discovered by Baxter and Griffin in 1905 when washing with potassium salt solutions a precipitate of ammonium molybdophosphate (AMP) used for the gravimetric determination of phosphorus[1]. However, this phenomenon was not widely used until the late 1950's and early 1960's, when it was applied to the concentration and separation of alkali metal ions[1-26], and to the determination of caesium in sea water and in effluents[27-30] and in biological materials[31-33]. It was then realised that insoluble HPA salts are valuable inorganic ion exchangers: they are cheap, readily available, and easily prepared in any laboratory. They can be used in theoretical studies of ion exchange processes[8] because they are monofunctional when suitably prepared and, like zeolites, they do not swell significantly in aqueous solutions.

Together with the experimental papers began to appear papers on the mechanism of sorption processes HPA salts[7,8,13-20,34-43] as well as review articles[1,2,4,44]. However, the most interesting of these reviews[1] is already more than 10 years old, and more recent reviews are either too sketchy[2,4] or inaccessible[44].

Furthermore, all the reviews published so far adopt a formal classification of the sorbed ions into univalent, bivalent, and multivalent to describe the mechanism of sorption processes. Univalent and bivalent ions have almost identical sorption mechanisms, and the substantial differences in sorption behaviour of the other ions are not revealed by classifying them all as "multivalent". We have therefore attempted to develop a more rational description of the sorption mechanism of various ions on HPA salts by combining two types of information: published data on the structure, formation conditions, and stability of the heteropoly compounds of different

elements, and observations on the sorption properties of HPA salts.

II. STRUCTURAL PROPERTIES OF THE HPA SALTS USED AS INORGANIC SORBENTS

Insoluble salts of heteropoly acids are inorganic sorbents with a fairly complex crystal structure[1-4]. The structural features of the initial heteropoly compounds (HPC) are responsible for the complexity of the processes at the sorbent–solution interface, and they should not be overlooked when the experimental results are analysed. We shall therefore examine the structure of a range of heteropoly compounds before attempting to describe the mechanism of ion exchange on HPA salts.

Of the many sparingly soluble HPA salts, ammonium molybdophosphate is most widely used as a sorbent. It is a HPC of the 12th series[45], having the Keggin structure[46-48]. Ammonium molybdophosphate is precipitated from aqueous solutions as fine yellow crystals of the neutral salt $(NH_4)_3 \cdot PMo_{12}O_{40} \cdot nH_2O$ or of the acid salt $(NH_4)_2HPMo_{12}O_{40} \cdot nH_2O$ (depending on the ratio of molybdophosphoric acid to ammonium salt)[49].

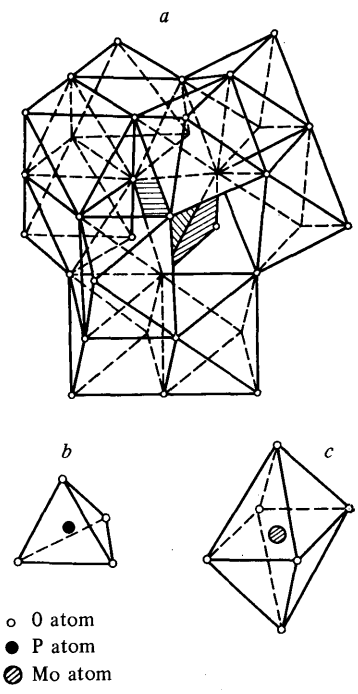


Figure 1. Structure of the $PMo_{12}O_{40}^{3-}$ ion[46]: (*a*) overall shape of the anion, (*b*) PO_4 tetrahedron, (*c*) MoO_6 octahedron.

Heteropoly compounds differ from ordinary coordination compounds in not having discrete ligands coordinated to a central atom. Therefore the coordination sphere of the HPC can be treated as a single complex ligand. At the centre of a ligand anion having the Keggin structure we find a PO_4 [46-48] tetrahedron (Fig.1), surrounded by twelve MoO_6 octahedra arranged in four groups of three: within each triplet the octahedra are edge-sharing, and the triplets are interconnected by sharing corners. Because of the electrostatic interaction between the atoms the octahedra are distorted, with different Mo–O distances. The structure is characterised by the presence of twelve Mo=O double bonds (oxygen end-atoms), and twelve almost linear and twelve angular Mo–O–Mo bridging bonds (bridging oxygen atoms). The HPA anion as a whole is an almost spherical particle with a negative charge (–3) on its surface. In the crystalline state there is no direct bond between the anions: the structure is stabilised by hydrogen bonds, or by the cations. All HPC can form a variety of crystal hydrates, in which the amount of water is often difficult to determine exactly[47,48]. Heteropoly acids and their salts with a Keggin structure crystallise in the cubic system[46,50]. The HPA anions retain their high symmetry in aqueous solutions[48,51]. In the crystalline salts the cations are accommodated in the spaces between anions, and they can exchange with cations in solution if their size allows[1,48].

Heteropoly compounds with the Keggin structure have the general formula[48] $E^{x+}M_{12}O_{40}^{x-8}$, where M is usually Mo or W, and E = B, Si, P, As, Cr, Mn, Fe, Co, Cu, Zn, Ti, Zr, Ga.

In addition to the simpler heteropoly compounds, a whole series of mixed HPC (in which one or more molybdenum atoms are replaced by Tungsten, vanadium, or another metal) has been synthesised[48]. The formation of mixed compounds is due to the general tendency of these ions to combine in polymeric structures, giving compounds which in most cases can be classified as complexes with the Keggin structure.

Triple complexes[48] are formed when highly charged ions (for example, Zr^{IV}, Ti^{IV}, Th^{IV}, Nb^{V}) are added to heteropoly acids in solution. The i.r. spectra of the solid complexes[52,53] show that zirconium, titanium, and thorium can replace molybdenum in the coordination sphere, forming mixed heteropoly complexes. Under these conditions the Keggin structure is retained.

Furthermore, we know from the chemistry of heteropoly compounds[48,54] that addition of alkali to a solution of (say) 12-tungstophosphoric acid produces an 11-tungstophosphate. These "unsaturated" compounds, for example the anion $EW_{11}O_{39}^{n-}$, have an incomplete Keggin structure in which one tungsten atom and one oxygen end-atom are missing[55]. The charge on the anion is always increased by four units. Some lanthanide and actinide ions can form stable complexes with unsaturated heteropoly complexes: the formation of these complexes with thorium[56], cerium[55], and other elements[57] has been reported.

Thus, several variants of the interaction of sorbed ions with ammonium molybdophosphate or other sparingly soluble salts of a HPC of the 12th series are possible.

1. As stated above, the cations in the salt structure are located in the spaces between the anions, and they can (if their size allows it) exchange with cations in the bulk of the solution[1]. Therefore, one variant of the interaction is the replacement of cations from the outer sphere of the sorbent by sorbed ions (i.e. the normal ion exchange reaction).

2. Since the HPA anions are not inert as a matrix, the sorption of ions tending to form mixed complexes with the molybdenum or tungsten of the coordination sphere can cause replacement of molybdenum or tungsten atoms by the corresponding metal atom.

3. Another possible variant is the adsorption of a metal ion on the surface of the anion in a geometrically favourable position, due to interaction with an oxygen end-atom. This interaction should be enhanced by the partial decomposition of the 12th-series HPA anion at high pH, giving a small amount of 11th-series HPA anions.

The most frequently used sorbents are sparingly soluble salts of 12th-series heteropoly acids with a Keggin structure: on these materials differences in sorption properties, and hence also in the possibility of separating various ions, are

determined mainly by the properties of the ions being sorbed, both physical (ionic radius, ionic potential) and chemical (state of the ion in solution, tendency to form complexes in general, and formation of heteropoly compounds in particular).

On the basis of their ability to form heteropoly compounds the inorganic ions can be classified into three groups.

I. The first group includes the ions which cannot normally act as complex-forming hetero-atoms, or form the coordination sphere of HPA, but which form salts with heteropoly acid anions. These are the ions of the alkali and alkaline-earth metals, many doubly charged ions such as Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, and Cd^{2+}, and some triply charged ions. These ions, if their size allows it, can exchange with the cations of sparingly soluble HPA salts, which behave towards them as ordinary strongly acidic cation exchangers.

II. The second group consists of ions which can act as the central atom in HPC. They include Ge^{IV}, Ti^{IV}, Zr^{IV}, Th^{IV}, Ce^{IV}, Te^{IV}, Se^{IV}, Ga^{IV}, Cr^{III}, Fe^{III}, Co^{II}, etc. Typical complex-forming ions with a high charge and a small radius, such as Ti^{IV}, Zr^{IV}, Th^{IV}, Ce^{IV}, Te^{IV}, etc., can interact with the anionic part of the sorbent by an addition reaction, especially in the presence of structural defects on the surface (partial degradation of the 12th-series HPA with formation of unsaturated compounds). The sorption of ions such as selenium, able to form highly stable HPC, can lead to reconstruction of the whole surface structure of the sorbent. However, all these ions can also take part in exchange in the outer sphere of the HPA salts as one of the steps in the sorption process.

III. The third group consists of ions able to form the coordination sphere of heteropoly compounds, such as molybdenum(VI), tungsten(VI), vanadium(V), and chromium(VI). Sorption of these ions by HPA salts is often accompanied by the formation of mixed heteropoly compounds.

This classification is not absolute, because some ions could be assigned to two of the groups with equal justification. For example, in the case of iron(III), salt formation with HPA anions has been reported[45] as well as the formation of heteropoly complexes in which the iron is the central atom[48]. Niobium can act as the central atom, forming molybdenum–niobium HPA,[48] but it can also form heteropoly compounds by entering the coordination sphere[47]. We should also note that in real systems it is rare to find one of the above types of interaction in a pure form: sorption process on HPA salts are usually complex. This statement is consistent with a large volume of recently published work.

III. SORPTION OF METAL IONS ABLE TO FORM SALTS WITH HPA ANIONS

Many salts of heteropoly acids have been described[45]. In the case of molybdophosphoric acid (MPA) and tungstophosphoric acid (TPA) the salts of the alkali and alkaline earth metals, and those of silver, thallium, and mercury(I) are known, as well as those of manganese, cobalt, nickel, cadmium, copper(I), iron(III), and zinc. All these ions can be assumed to undergo exchange, to varying extents, on the insoluble salts of heteropoly acids. For the separation and concentration of ions the product of the interaction of the sorbed ion with the initial, sparingly soluble HPA salts must also be insoluble, i.e. the ammonium ions in the AMP structure can be exchanged to a significant extent only for metal ions which form HPA salts insoluble in water[7].

Healy's work[49,58,59] is highly relevant to the identification of the range of ions which can form sparingly soluble salts with HPA anions: he prepared and analysed the neutral and the acid salts of the alkali metals, silver, thallium(I), mercury(I), and barium, and also some mixed salts of alkali metals and of barium with aluminium, iron(III), and some rare-earth elements, with the anions of MPA, TPA, and tungstosilicic acid. Healy concludes from a study of the solubility of these salts[59] that mixed salts prepared by exchange of ions in the outer sphere of HPA are sparingly soluble if two of the three hydrogen atoms in the MPA or TPA are replaced by a heavy alkali metal, while the third hydrogen atom can be replaced by a light ("soluble") or a heavy ("insoluble") alkali metal. For example, the salts $K_2LiW_{12}O_{40}$ and $K_2RbW_{12}O_{40}$ have a very low solubility in water. Salts of the alkaline-earth metals are more soluble in water(and even more so in acids) than the salts of the heavy alkali metals, and therefore they are not absorbed by tungstophosphates at acidities above 0.3 M, though they can be easily removed from solutions at pH 1–4.[59]

From the point of view of solubility the most effective use of the ammonium salts of HPA is exchange with heavy alkali metal ions such as K^+, Rb^+, and Cs^+, or with the Tl^+, Ag^+, and Hg_2^{2+} ions, which form the least soluble salts with HPA.[49] For this reason HPA salts were first used as ion exchangers in the concentration and separation of heavy alkali metal ions[5–9]. A large amount of experimental information on the exchange of alkali metal ions on MPA and TPA salts is now available, and the mechanism of these processes has been studied in detail.

Smit and coworkers[5–8] carried out one of the first and most fundamental studies of this problem by synthesising the ammonium salts of various HPA,[7] calculating the distribution coefficients of several alkali metal anions, and analysing the results[7,8]. They established[7] that for a given HPA salt the distribution coefficient increases with the atomic number (or ionic radius) of the alkali metal, i.e. in the same order as in the case of strongly acidic organic ion exchangers. The higher distribution coefficients of Ag^+ and Tl^+ (as compared to alkali metal ions of the same size) are ascribed by Smit to the partial covalency of the bond between Ag^+ or Tl^+ ions and the HPA anions. The separation factors for pairs of alkali metal ions (defined as the ratio of the distribution coefficients under similar experimental conditions) are much higher for the ammonium salts of HPA than for the Dowex-50 resin. The selectivity of AMP towards heavy alkali metals is so great that small amounts of the larger alkali metal ions (Cs^+ and Rb^+) can always be selectively adsorbed from solutions containing amounts of the smaller alkali ions several times greater than the maximum capacity of the column[8]. Thus, 19 mg of Rb^+ can be quantitatively separated from 600 mg of K^+ on a column containing 1 g of AMP and 0.5 g of asbestos. The first attempt at relating the cation exchange properties of AMP and other HPA salts to their crystal structure was reported by Smit.

The basic parameter which determines the exchange of a univalent cation on AMP is, according to Smit, the ionic radius. The large alkali metal cations can be stably accommodated in the holes of the lattice and lower the lattice energy sufficiently to form sparingly soluble salts. It is suggested[7] that because of the pore structure of the HPA salts ion exchange can take place over the whole of the crystal lattice, and not just on the surface of the crystals. However, large organic cations cannot move freely through the lattice, and they are exchanged on the crystal surface only.

The validity of the law of mass action for exchange processes on MPA has been tested[8] by a study of the Rb^+–NH_4^+ exchange. By analysing the elution curves it was shown that not all the ammonium ions in AMP can be exchanged: ~60% of the ammonium ions can be replaced by caesium, and ~80% by rubidium. Smit explains this observation by postulating that caesium ions (and, to a lesser extent,

rubidium ions) can block the channels of the ions exchanger, thus hindering the diffusion of ions in the lattice.

However, subsequent work on the exchange properties of HPA salts has shown that the sorption of alkali metal is a more complex process. Thus, Krtil established[13-19,36] that in most cases the results apply to the acid salts of HPA. When the initial salts have the composition $(NH_4)_{2.67}H_{0.33}(PW_{12}O_{40})\cdot 9.8H_2O$ or $(NH_4)_{2.95}H_{0.05}(PMo_{12}O_{40})\cdot 11.6H_2O$ treatment with acid causes exchange of NH_4^+ ions by hydrogen ions, with formation of a more acid salt[9]. Later work showed[13,15,36] that the sorption of alkali metal ions on the salts of heteropoly acids can involve three independent processes: a) exchange of ammonium ions by alkali metal ions, b) exchange of hydrogen ions from the sorbent by alkali metal ions, c) exchange of ammonium ions from the sorbent by hydrogen ions from the acid solution.

The equilibrium constant for all these processes have been determined[36], and it has been shown that the exchange of alkali metal ions on HPA salts obeys the law of mass action. Mathematical treatment of sorption data using this law can be carried out relatively simply only when the sorbed ion is present in trace amounts (as compared with the ammonium ion or the acidic hydrogen of the sorbent[1]). In this case the plots of $\lg D$ against pH and $\lg D$ against $[NH_4]$ should be straight lines of unit slope. This expectation has been confirmed experimentally in studies of the sorption of alkali metal ions on HPA salts[5-36].

Table 1. Distribution coefficients D of different cations on AMP in 0.1 M NH_4NO_3.[34]

Cation	Li+	Na+	K+	Rb+	Cs+	Ag+	Tl+	H_3O^+
r, Å	0.60	0.95	1.33	1.48	1.69	1.26	1.40	—
D	0.57	0.78	4.7	266	4024	54	3939	0.84
θ_{max} %	20.9	26.4	48.7	53.6	45.3	64.8	45.8	—

Though the general features of the sorption of alkali metal ions on HPA salts are generally agreed, different workers report different experimental values of the distribution coefficients D and of the maximum extent of exchange of the ammonium ion in HPA salts by alkali metal ions. Thus, Krtil[18] determined the maximum sorption capacity of AMP and ammonium tungstophosphate (ATP) towards caesium: the results (1.0 and 0.66 mg-equiv Cs g^{-1} respectively) indicate the formation of the dicaesium salt of the HPA in both cases. On the other hand, measurements of the maximum extent of exchange (θ_{max}) of the ammonium ions by alkali metal ions under dynamic conditions[34] did not give values of 33.3 and 66.6%, corresponding to the exchange of one or two ammonium ions (Table 1). The differences between the D values obtained by different workers[8,15,18,34,36] can be ascribed to different experimental methods and different procedures for the preparation of the sorbent.

A detailed study[18] of the sorption of caesium and rubidium on normal and on acid ammonium and thallium salts of MPA and TPA revealed some interesting features: thus, caesium in weakly acidic solutions (0.01 M HNO_3) has a lower affinity for the acid salt than for the normal salt. A possible explanation is that in normal ammonium salts of HPA the caesium can be exchanged only by ammonium ions, whereas in acid salts it can be exchanged by NH_4^+ and H^+ ions. Measurements of the pH dependence of the sorption of caesium on acid salts at constant concentration of ammonium ions have shown that the process is influenced by hydrogen ions only at acidities ≥1 M (in HNO_3). Hence, caesium can exchange with hydrogen ions only in strongly acid solutions.

Attempts have been made[34,35] to relate the sorption of alkali metal ions to various physicochemical characteristics of AMP and of the sorbed ions. Thus, it has been shown[35], by analysing the solubilities of the corresponding HPA salts and their crystal lattice energies, that the separation of alkali metal ions on AMP is possible in principle. The affinity series obtained from that work, $Cs^+ > Rb^+ > K^+$, is consistent with the more general sequence[34]

$$Cs^+ = Tl^+ > Rb^+ > Ag^+ > K^+ > H^+ > Na^+ > Li^+,$$

shown in Table 1. Furthermore, we note a linear relationship between $\lg K'$ (where K' is the equilibrium constant of the exchange reaction) and ΔH (the energy of hydration) for Cs^+, Rb^+, and K^+, whereas the smaller ions Na^+ and Li^+ have unexpectedly high values of $\lg K'$. It is suggested[34] that the smaller alkali metal ions undergo exchange in a partially hydrated form (Fig.2). By applying the law of mass action to the experimental exchange isotherms for the alkali metal ions an isotherm equation valid over a wide range of concentration has been obtained[34]. It assumes that the activity of the ammonium ions in the crystal is equal to the mole fraction of exchangeable ammonium ions, and that the ions in the solid phase are in an ideal solution. Thus, the equation is an analogue of the Langmuir isotherm[60]. The agreement between experimental and calculated results is satisfactory.

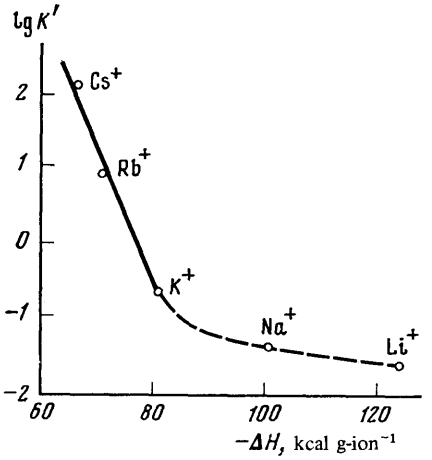


Figure 2. Logarithm of the equilibrium constant of the exchange reaction against hydration energy of the alkali metal ions[34].

One of the early publications[6] suggested the following mechanism for the exchange of bivalent ions (in particular, barium) on AMP:

$$Ba^{2+} + H_2O \rightleftarrows Ba(OH)^+ + H^+ \quad (1)$$

$$RNH_4 + Ba(OH)^+ \rightleftarrows RBa(OH) + NH_4^+ \quad (2)$$

where R is a molybdophosphate anion. The evidence for this conclusion was that only large univalent cations are readily exchanged with the ammonium ions of AMP, and the ion $Ba(OH)^+$ satisfies both conditions (univalence, and large crystallographic radius). Furthermore, this reaction scheme

explains the dependence of the sorption of barium on the concentration of ammonium ions as well as on the acidity of the medium.

More recent work[14,27,61] in different laboratories on the sorption of ^{90}Sr on various HPA salts led to the conclusion[14] that $\lg D$ for strontium varies linearly with pH at pH < 3, with a slope of −2 (i.e. one strontium ion is exchanged for two hydrogen ions). These experimental facts cannot be explained by Smit's mechanism[18]. Healy[59] critically examined Smit's mechanism, and pointed out that a species such as $Ba(OH)^+$ is highly unstable, and very unlikely to exist in bivalent cation salt solutions under the conditions used for sorption on AMP. Smid himself came to the same conclusion in a later paper[62]. Referring to Stockdale's results[63], Smit pointed out that even in weakly acid solutions the sorbent is in the form of an acid salt of MPA, of composition intermediate between the doubly and the triply substituted salt. The pure doubly substituted salt can be prepared by washing the exchanger with acid[58,63]. Smit concluded from these observations that bivalent ions are sorbed reversibly on AMP by exchanging with ammonium ions or with the oxonium ions remaining in the AMP precipitate in spite of thorough washing with ammonium nitrate:

$$2\,(NH_4)_2\,(H_3O,\,NH_4,\,Na\ \text{ etc.})\,MP + Ba^{2+} \rightleftarrows \rightleftarrows [(NH_4)_2\,MP]_2\,Ba + 2\,(H_3O^+,\,NH_4^+,\,Na^+\ \text{etc.}) \qquad (3)$$

This reaction scheme is consistent with the dependence of the sorption of bivalent ions on pH and on the concentration of ammonium ions, and also with the slope of the plots of $\lg D$. Furthermore, it is clear that the exchange mechanisms of univalent and bivalent ions on HPA salts must be similar, and there are no grounds for involing specific mechanisms in the two cases as is often done in the literature[1,6,62,64]. However, there is a difference in the sorption and elution conditions of the two types of ion, and this difference has been used in the separation of ^{137}Cs and ^{90}Sr.[6,14,27,36,61,62] It is probably associated with the differences in solubility of the exchange products in water and in acid solutions[49,58,59].

Table 2. pH of the equilibrium solutions before (pH_1) and after (pH_2) contact with AMP.[64]

M^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
pH_1	5.89	6.20	6.30	6.54	6.37	6.19	6.33	4.88	5.37	6.14
pH_2	3.87	3.55	3.41	3.03	3.74	3.50	3.49	3.26	3.48	3.53

The sorption of Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Hg^{2+} has been studied[64] under both static and dynamic conditions. The D values are independent of acidity at pH > 3 for practically all the listed ions, and in more strongly acidic solutions they increase with pH. The variation of $\lg D$ with $\lg [NH_4NO_3]$ is a straight line of unit slope. From these observations the authors conclude[64] that the exchange with ammonium ions involves a singly charged particle, possibly $M(OH)^+$: in other words, they revert to the Smit mechanism[6], described by Eqns.(1) and (2). Though the $M(OH)^+$ complexes are unstable for most of these ions, it is suggested[64] that the equilibrium of their formation reaction (1) is shifted towards the right by the sorption of $M(OH)^+$ particles on the AMP. The observed decrease in pH of the equilibrium solutions during sorption of bivalent ions on AMP (Table 2) is quoted[64] as evidence for the validity of Eqns.(1) and (2).

However, a lowering of the pH of the equilibrium solution can be produced also by the exchange mechanism corresponding to Eqn.(3) if the sorbent is an acid salt of MPA. The authors[64] had worked with a normal salt, and therefore they excluded the possibility of exchange by the mechanism (3). However, they controlled the composition of their sorbents by determining the AMP content alkalimetrically rather than by determining the ammonia content. Because of the large molecular weight of the molybdophosphate anion (as compared to NH_4^+, and even more so as compared to the hydrogen ion) this approach cannot give accurate results. The most convincing argument in favour of exchange by Eqns.(1) and (2) is the slope of the plots of $\lg D$ against $\lg [NH_4NO_3]$, and also the pH value of the solutions before sorption (greater than 5 in every case, see Table 2). The $M(OH)^+$ particles may be relatively stable under these conditions.

Table 3. Distribution coefficients of trace amounts of doubly charged cations on AMP in 0.1 M NH_4NO_3 solution[64].

M^{2+}	D	M^{2+}	D	M^{2+}	D
Mg^{2+}	0.81	Mn^{2+}	1.34	Cu^{2+}	1.92
Ca^{2+}	1.48	Co^{2+}	1.38	Zn^{2+}	4.28
Sr^{2+}	1.34	Ni^{2+}	1.77	Cd^{2+}	2.21
Ba^{2+}	3.68				

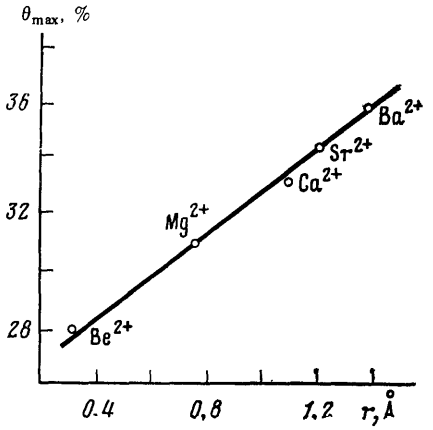


Figure 3. Maximum exchange (θ_{max}) of alkaline-earth ions against ionic radius[64].

The stoichiometry of the exchange was tested[64] by a series of dynamic experiments aimed at determining the maximum capacity of the column for different bivalent cations: the result was that different cations can replace different amounts of ammonium ions in AMP. For example, in the exchange of Hg^{2+} ions ~10% of the ammonium ions are replaced, as compared to 27% in the exchange of Zn^{2+}, 23.5% in the exchange of Co^{2+}, etc. These values differ very substantially from the values (33.3 and 66.6%) corresponding to the stoichiometric exchange of one or two ammonium ions. With the alkaline-earth metal ions a direct proportionality is found between the maximum degree of exchange and the ionic radius (Fig.3), but not with other ions.

The distribution coefficients for trace amounts of bivalent[64] and univalent ions[34] have also been determined (under otherwise identical conditions). We note (Table 3) that the distribution coefficients for bivalent ions are much smaller than those for the heavy univalent ions. From the experimental results the bivalent ions can be arranged in the following affinity series:

$$Zn^{2+} > Ba^{2+} > Cd^{2+} > Cu^{2+} > Ni^{2+} > Ca^{2+} > Mn^{2+} \sim Sr^{2+} \sim Co^{2+} > Mg^{2+}.$$

IV. SORPTION OF IONS ABLE TO ACT AS THE CENTRAL ATOM IN HETEROPOLY COMPOUNDS

This is the most extensive group of ions in our classification. As was pointed out in Section II, it includes the typical complex-forming ions, such as Ce^{III}, Y^{III}, Sc^{III}, Fe^{III}, Cr^{III}, Ti^{IV}, Zr^{IV}, Th^{IV}, Ce^{IV}, Te^{IV}, Ga^{IV}, Nb^{V}, U^{VI}, U^{IV}, Np^{IV}, etc. Many of these ions carry a high charge and have a small radius, i.e. they have a high ionic potential, which explains their highly developed tendency to form complexes. All these ions can act as the central atom in heteropoly compounds. The heteropoly complexes of Ti^{IV}, Zr^{IV}, Cr^{III}, and Fe^{III} have the Keggin structure[48,65].

Hexamolybdenum and hexatungsten compounds with octahedral coordination of the central atom, of general formula $E^{x+}M_6O_{24}^{x-12}$, are formed by ions such as Te^{IV}, Al^{III}, Cr^{III}, Fe^{III}, Ga^{III}, etc.[48,66,67]

The structure of the heteropoly complexes of Ce^{IV}, Th^{IV}, U^{IV}, and Np^{IV} has been described[48,68-71]. It has one special feature: the central atom has icosahedral surroundings. This structure is now called the Dexter–Silverton structure[72], and the anion has the general formula $E^{4+}M_{12}O_{42}^{8-}$. "Triple" heteropoly complexes have been described for many ions of this group. They have been used in the spectrophotometric determination of titanium[73-77], thorium[78,79], zirconium[80], niobium[81,82], hafnium[83], yttrium[84], nickel[85], and other elements. Opinions as to the location of the second hetero-atom in such a structure have varied. The earlier papers[73-75,80,81,83] suggested that the third component occupies a special place in the coordination sphere rather than replacing molybdenum, thus acting (with the phosphorus) as a second central atom. More recently the most generally held view has been that the triple complexes are mixed heteropoly compounds, in which some of the molybdenum is replaced by another element[48].

On the other hand, some of the ions listed above can also form salts with HPA anions. In particular, Healy[59] has described the formation of mixed cerium–caesium $[(Cs_2PW_{12}O_{40})_3Ce]$, aluminium–caesium $[(Cs_2PW_{12}O_{40})_3Al]$, and iron–caesium $[(Cs_2PW_{12}O_{40})_3Fe]$ salts of tungstophosphoric acid. The same paper describes the formation of mixed salts of ammonium and caesium with cerium, praseodymium, and europium during the sorption of the latter elements on precipitated ammonium and caesium molybdophosphates.

The cations do not occupy a fixed position in the structure of the heteropoly acid salts[47,48,86], and they are merely accommodated in the space between the anions. If their size allows, they can be exchanged for cations from the external solution[1,7,8]. Hence, the first step in the sorption of cations on sparingly soluble heteropoly acid salts is diffusion into the crystal and exchange with the cations of the salt. In the first group of cations, discussed in Section II of this review, these steps conclude the process, and mixed salts of the appropriate HPA are formed. On the other hand when the sorbed ions can act as the hetero-atom in an HPA it can also (under suitable conditions) interact further with the anion, which can no longer be treated as an inert matrix (as in the exchange of alkali or alkaline-earth metals).

Before discussing the possible types of interaction between the sorbed ions and the anions of HPA salts we should examine the experimental information on the sorption of these ions on molybdophosphates and tungstophosphates. The sorption of ions in this group has been studied for many years merely from the standpoint of separating these ions from alkali metal ions (for example, in the preparation of radiochemically pure caesium-137 [6,11,17,19,22] or potassium-42.[24]) Krtil[36] and Smit[62] were among the first to study the sorption mechanism of tervalent ions.

Krtil believes[36] that the interaction of yttrium(III) and cerium(III) with ammonium tungstophosphate is based on ion exchange with the ammonium or hydrogen ions of the sorbent. At nitric acid concentrations of 0.2–1 M Krtil observed a linear relationship between $\lg D$ and $\lg c_{HNO_3}$, with a slope of 3, from which he concluded that yttrium and cerium(III) are exchanged for three hydrogen ions at these acidities. The bond between the sorbed ions and the sorbent is relatively weak, since these ions can be displaced by hydrogen ions. The pH for maximum sorption is ~1. Furthermore, Krtil suggests that the sorption of these ions (in contrast to the sorption of alkali metal ions) does not depend on diffusion of sorbate into the sorbent lattice, since all the processes are confined to the surface of the sorbent.

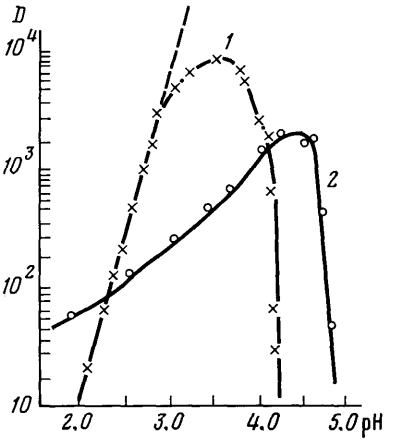


Figure 4. Distribution coefficient of yttrium from 0.1 M NH_4NO_3 solution against acidity of the medium[62]: *1*) on AMP, *2*) on ATP.

Smit[62] studied the pH dependence of the sorption of yttrium on AMP and ATP. Like Krtil[14], he found a fairly complex dependence (Fig. 4), the slope in the pH region 2–3 (curve *1*) being 2.72 instead of the expected 3.0. The distribution coefficients were determined after stirring the yttrium solution with the sorbent for 10–12 h. As Fig. 4 shows, when the pH of the equilibrium solution is increased above 3 the sorption of yttrium on AMP falls off sharply. By comparing these results with those of dynamic experiments Smit discovered some interesting discrepancies. In the dynamic experiments some of the yttrium sorbed at pH < 4 can be eluted (together with strontium) by a 1 M solution of NH_4NO_3, whereas elution of the remainder requires a solution

of 1 M NH_4NO_3 + 1 M HNO_3. On the other hand, after sorption on AMP from an acetate buffer solution at pH 4.5 the whole of the yttrium is in a form which cannot be eluted by 1 M NH_4NO_3. This can be exploited for the separation of strontium from yttrium. The process is not easily reversible: rapid elution of the yttrium requires at least a 0.5 M solution of HNO_3. Smit believes that the yttrium which cannot be eluted by NH_4NO_3 is adsorbed on an unusual type of exchange centre, or by a special mechanism, so that the ion exchange reaction is complicated by some additional interaction in this case. It is suggested[62] that complex formation between the sorbed ions and various decomposition products of the heteropoly anion (or even the 12th series HPA themselves, structurally modified) can occur in the solid phase.

As stated, in Smit's experiments the equilibrium sorption fell off steeply at pH > 3, which at first sight cannot be reconciled with the results of dynamic experiments. However, it was shown that if the equilibrium experiments at pH > 3 are carried out in 1 min rather than 10–12 h the D values no longer decrease with increase of pH, but lie on an extension of the left-hand branch of curve *1* in Fig. 4 (broken line). The decrease in the distribution coefficients of yttrium at high pH values after relatively long equilibration times is ascribed[62] to complex formation between ytrrium in the aqueous phase and the soluble decomposition products of the 12-AMP (which may include the 11-molybdophosphate anion).

Unfortunately, kinetic sorption curves for yttrium are not given in Ref. 62, but the results of the following experiment are quoted. A sample of AMP was left overnight in contact with a 0.1 M solution of NH_4NO_3 in a pH 4.5 buffer (sodium acetate). The water phase (which had developed a yellow colour) was then separated, a trace of yttrium was added to it, and the solution was allowed to contact a fresh portion of AMP for 1 min. Under these conditions practically no sorption of yttrium was observed. On the other hand, when the first sample of AMP was immersed for 1 min in a fresh buffer solution (at pH 4.5) containing a trace of yttrium unusually high D values for yttrium were obtained.

It is suggested[62] that this experiment demonstrates the formation of water-soluble complexes which cannot be adsorbed on AMP. X-Ray diffraction patterns of AMP samples exposed for 20 h to a pH 4.5 buffer solution are taken as evidence that the AMP samples are unchanged. The present writers find this evidence unconvincing, since one of the most likely decomposition products of 12-molybdophosphate is the 11th series anion, which consists (see Section 1) of an incomplete Keggin structure with a missing molybdenum atom and oxygen end-atom[55]. The presence of a few structural defects of this type on the sorbent surface can hardly be detected by X-ray diffraction analysis. Therefore, we believe that the type of interaction between yttrium and the molybdophosphate anion in the solid phase is still an open question.

As regards the other ions of this group, the sorption of titanium, thorium, uranium, neptunium, zirconium, niobium, selenium, and tellurium on various heteropoly acid salts has been investigated[37–43,87–93]. Sorption processes involving these elements may be even more complex than with yttrium, because these multiply charged ions tend to hydrolyse in aqueous solutions as well as forming many types of complex with anions of different acids. Allowance for all these factors (in addition to the possible interactions with the anionic part of the sorbent) must be made in studies of the sorption processes for these ions.

Thus, in a study of the behaviour of uranium(VI) during sorption on AMP the hydrolysis of the ion and the formation of nitrato and sulphato complexes had to be allowed for[38]. At low concentrations of HNO_3 (<10^{-2} M) and NH_4NO_3 (<5 × 10^{-3} M) the distribution coefficient of the uranyl ion on AMP ($\lg D$) was found[38] to be independent of the concentration of HNO_3 and NH_4NO_3, but at higher concentrations a linear relationship with a slope of unity was observed. These results led to the conclusion[38] that in the ion exchange reaction a univalent ion replaces an ammonium ion, the most probable exchanging particle in this case being UO_2OH^+. Exchange of the $UO_2NO_3^+$ particle is said to be impossible, because its formation occurs at higher concentrations of nitric acid than those used in this work (0.01–0.25 M). The sorption mechanism of the UO_2OH^+ ion is equated[38] to that of alkali metal ions, an ammonium or hydrogen ion in the AMP being replaced by the UO_2OH^+ ion. The law of mass action was shown to apply to exchange equilibria involving uranyl ions present in solution in different forms. The sorption of uranium is reversible: under dynamic conditions the uranium is sorbed from a 10^{-3} M solution of nitric acid and eluted in 100% yield by a 1 M solution of the acid.

The sorption of elements such as zirconium and niobium has been studied for many years merely with the aim of optimising their separation from caesium-137.[17,19,22,36] It was shown[17,36] that the behaviour of zirconium and niobium differs very substantially from that of the other fission products. Though the plot of $\lg D$ against $\lg c_{HNO_3}$ is linear, its slope is fractional. Krtil suggests[36] that in this case molecular sorption of neutral complexes or hydrated forms of the elements must be taking place. Because of the low solubility of zirconium phosphates he concludes that the anomalous behaviour of zirconium and niobium is due to chemisorption. Under the conditions used for the sorption of alkali metal ions the sorption of zirconium and niobium is partially irreversible. If the initial solution contains hydrofluoric acid, the elements are converted into fluoro complexes and are sorbed with difficulty: only 0.01% of a ^{95}Zr–^{95}Nb mixture is extracted under these conditions[19]. Solutions containing tartaric acid[22] as well as HF are recommended to minimise the sorption of these isotopes.

In a more recent paper[89] the same workers describe in detail the sorption mechanism of zirconium and niobium, allowing for the formation of hydrolysed and polymerised forms of these elements in aqueous solutions. Both elements give rise, in acid solutions, to chemical forms which can be sorbed on AMP both by ion exchange (cations) and by adsorption (neutral molecules, and colloidal particles). Addition of neutral salts was found to affect the sorption of zirconium and niobium on MPA, the distribution coefficients increasing with the concentration of ammonium and sodium ions, whereas under ion exchange conditions ammonium ions lower the sorption coefficients by taking part in the exchange equilibrium. Hence, the sorption of trace quantities of zirconium and niobium on AMP involves adsorption of hydrolysed or polymeric forms of these elements rather than ion exchange (as in the case of caesium). Complexing agents decrease the sorption of both elements by hindering the formation of strongly sorbed polymeric forms. The effect of complexing agents on the sorption of ^{95}Zr increases in the sequence $NO_3^- \ll$ tartrate ≅ citrate ≅ $SO_4^{2-} < F^- \cong$ oxalate, and for ^{95}Nb the series is citrate ≅ tartrate ≅ $NO_3^- \ll SO_4^{2-} < F^- \cong$ oxalate.

The sorption of microgramme quantities of niobium on the caesium and ammonium salts of MPA was first studied[87] with the aim of separating niobium from a large excess of titanium. As in the case of trace amounts of ^{95}Nb,[89] the niobium is not desorbed by solutions of mineral acids, but it can be eluted quantitatively by 40 ml of a solution of NH_4F (0.2 M) at pH 2. Hence, and also in view of the considerable sorption of niobium from acid solutions and of the failure of ammonium

and sodium ions to influence the sorption, the interaction of niobium with HPA salts cannot be purely by ion exchange. Titanium is less strongly held by caesium molybdophosphate: it is not sorbed at an acidity >0.5 M HCl, and it can be desorbed quantitatively by a 5 M solution of HCl. The differences in behaviour of niobium and titanium can be used to separate these isotopes[87].

The sorption of thorium on ammonium molybdophosphate was first described by Ganzerli-Valentini and coworkers[37]. Their measurements (under static conditions at room temperature) included the effect of factors such as the concentration of nitric acid, time, and the concentration of ammonium nitrate on the distribution coefficient of thorium (D_{Th}) on AMP. By studying the dependence of D_{Th} on the time of shaking the solution with the sorbent it was found that equilibrium in solutions 10^{-3} M and 0.7 M with respect to HNO_3 is reached in 12 and 8 h respectively. The plot of $\lg D_{Th}$ against concentration of nitric acid is fairly complex (Fig.5): at nitric acid concentrations below 0.3 M the dependence is non-linear, but the experimental points for 0.3–1 M HNO_3 lie on a straight line of slope −3.7. The maximum value of D_{Th} is 13500. The linearity of the plot of $\lg D_{Th}$ against $\lg [HNO_3]$ denotes that in this region of $[HNO_3]$ values of Th^{4+} ion is replacing the acidic hydrogen of AMP by an ion exchange mechanism. The deviation of the slope from an integral value was first ascribed[37] to experimental error, but in view of the reproducibility of the measurements the authors then concluded that the activity of thorium in solution may be affected by the concentration of nitric acid through the formation of nitrato complexes.

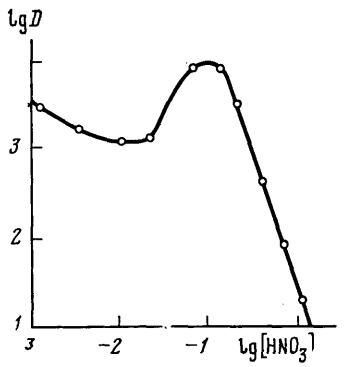


Figure 5. Distribution coefficient of thorium on AMP against the acidity of the medium[37].

The authors[37] do not reach a firm conclusion on the sorption mechanism of thorium for $[HNO_3] < 0.3$ M, though they suggest the possibility of formation of thorium hydrolysis products, or of complexes of thorium with molybdophosphoric acid or its decomposition products. It is not stated whether these complexes are formed in the liquid phase or in the ion exchanger, but nevertheless the slow equilibration in a 10^{-3} M HNO_3 solution (as compared with 0.7 M HNO_3) is ascribed to the formation of these complexes.

The following dependence of $\lg D_{Th}$ on the concentration of ammonium nitrate was observed (Fig.6): between 5×10^{-3} and 1.5×10^{-2} M NH_4NO_3 the plot is linear, with a slope of −4, confirming that the interaction of thorium with AMP is by an ion exchange mechanism, but for $[NH_4NO_3] > 1.5 \times 10^{-2}$ M there is a change in slope which the authors[37] ascribe (as in the case of nitric acid) to a change in the activity of thorium ions in solution. In all the equilibrium experiments the pH was measured in the initial solutions as well as at equilibrium. In every case the pH of the equilibrium solution was found to be lower by ~0.1 pH unit, confirming that the acidic hydrogen of the sorbent is involved in the exchange.

With thorium, uranium, and neptunium the experiments under dynamic conditions show a hysteresis effect[40] which had been briefly mentioned in Ref.37. Whereas thorium is sorbed on AMP from 10^{-3} M HNO_3, its removal from the column begins at a concentration of 0.5 M HNO_3, and does not go to completion. A mixture of 1 M HNO_3 + 1 M NH_4NO_3 removes 70% of the thorium, and a 2 M HNO_3 + 1 M NH_4NO_3 solution removes 90%. Increasing the concentration of ammonium nitrate has little effect on the elution of the thorium, but by increasing the concentration of acid we can remove the thorium from the column quantitatively (at 8 M HNO_3). If sulphuric acid is used as the eluent the thorium can be washed out of the column at a lower concentration of the acid.

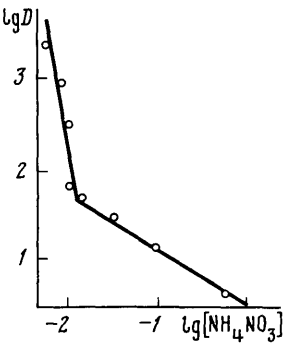


Figure 6. Distribution coefficient of thorium on AMP against concentration of NH_4NO_3 (in 0.1 M HNO_3). [37]

Np(IV) behaves in many ways like Th(IV) during sorption on AMP. The shift of the linear portion of the $\lg D_{Np}$ against $\lg [HNO_3]$ plot towards acidities greater than in the case of thorium is explained[39] by a higher tendency towards hydrolysis. In the region of 0.5–2.5 M HNO_3 the slope of the linear portion denotes exchange of a Np(IV) particle. However, at lower acidities the sorption of Np(IV) is no longer described by an ion-exchange reaction. Experiments under dynamic conditions[40] have shown that the sorption of Np(IV) on AMP is even more irreversible than that of thorium: even 14 M nitric acid cannot elute more than 87% of the neptunium.

It has been confirmed experimentally[40] that thorium, neptunium, and (to some extent) uranium can form complexes with molybdophosphate or its decomposition products under the conditions needed for the sorption of these elements on AMP. It is not stated[40] whether these complexes are formed in the solid or in the liquid phase. However, it is suggested that the AMP lattice may be distorted by the small size and high charge of the Np(IV) and Th(IV) ions, causing an increase in the rate of decomposition of the AMP, but the influence of these changes on the distribution coefficients of the sorbed ions is not made clear.

The maximum in the plot of the sorption of neptunium(IV) against time of contact between the phases (Fig.7) is explained[39] by postulating that the Np(IV) ions initially adsorbed on the AMP surface can form complexes with the heteropoly anions which are then returned (in part) to the solution. The possibility of complex formation in the solid phase is specifically mentioned in order to explain the difference between the slope (−2) of the plot of $\lg D_{Np}$ against $\lg [NH_4NO_3]$ and the expected value (−4), and also the almost total irreversibility of the sorption of Np(IV) under dynamic conditions[40].

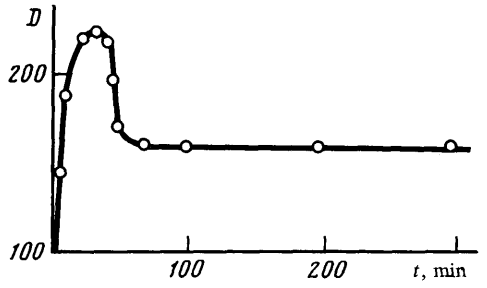


Figure 7. Distribution coefficient of neptunium(IV) on AMP against time of contact between the phases[39].

In an attempt to clarify the treatment of the sorption mechanism of thorium on AMP the writers have shown[43] that the dominant process at pH 0–1.15 is ion exchange of the thorium for the ammonium or the acidic hydrogen of the sorbent. Further evidence for this conclusion comes from the dependence of the distribution coefficient of thorium on AMP on the concentration of phosphate and molybdate ions in solution at pH 0.7: the phosphate ions have almost no effect on the sorption of thorium, whereas addition of molybdate ions to the solution gives a lower value of D_{Th}. This can be explained by postulating the formation by thorium in aqueous solutions of molybdenum–thorium heteropoly complexes of an anionic type[69], which cannot be sorbed in the outer sphere of the AMP.

Simultaneously present phosphate and molybdate ions have a more marked effect than molybdate ions alone. The measurements were made at pH 0.7, which corresponds to the optimum conditions for the formation of the soluble thorium–phosphorus–molybdenum triple complex[78] (of the anionic type). Since under the present conditions the triple complex is more stable than the double (thorium–molybdenum) complex, the sorption of thorium on AMP is almost totally suppressed by the presence of the phosphomolybdate reagent. Hence, the sorption of thorium on AMP is hindered by the formation of heteropoly complexes in the aqueous phase. From the sorption isotherms on AMP at different temperatures[43] we find that the sorption of thorium on AMP increases with temperature, in contrast to the behaviour of true ion exchange systems. This effect sets in at high concentrations of thorium.

Thus, the ion exchange process is complicated by the interaction of thorium with the anionic part of the sorbent. In order to establish whether molybdenum is displaced from the coordination sphere of the AMP, or whether the metal is adsorbed on the anion surface as a result of interaction with an oxygen end-atom, the equilibrium solutions were analysed for molybdenum and phosphorus during the measurement of the isotherms. No correlation between the amount of sorbed thorium and the amount of molybdenum in solution could be found, and therefore any interaction between the thorium and the anionic part of the sorbent can only be of the addition type.

As was stated above, an increase in pH favours the decomposition of heteropoly compounds of the 12th series with formation of compounds of the 11th series[48,54]. Thorium can form relatively stable compounds with the latter[56]. Therefore we cannot exclude the possibility of an equilibrium between 11th- and 12th-series compounds on the surface of the sorbent in contact with the solution, the presence of the 11th-series compounds enabling the thorium to form complexes with the anionic part of the sorbent.

In the case of selenium and tellurium—the next members of this group of ions—kinetic measurements have shown[41] that sorption is accompanied by chemical interaction with the anionic part of the sorbent. The experimental results obey the equation for diffusion within the grain. In order to identify the rate-limiting step unequivocally the activation energies for the sorption of Se(IV) and Te(IV) on AMP were calculated (18.4 and 7.7 kcal $mole^{-1}$ respectively). These values confirm that diffusion in the grain is the slowest step in the process. When the chemical interaction between the ions and the sorbent is unhindered (small ionic radii, high concentration of sorbed ions, and long contact times between the sorbent and the solution) the kinetic curves no longer obey the diffusion equations. The presence of chemical interactions between the anion of the sorbent and the sorbed ion is confirmed by the lack of dependence of the rate of sorption of Se(IV) on the nature of the cation of the sorbent and on the concentration of electrolyte.

Studies of the sorption of Se(IV) and Te(IV) on AMP under equilibrium conditions have shown[42] that the hydrogen ions in the sorbent can contribute to the ion exchange process if the acidity of the solution is high enough. At higher pH values the value of D is unaffected by changes in acidity, suggesting chemical interaction between the sorbed ion and the sorbent matrix.

The exchange constants and thermodynamic exchange functions have been calculated from the sorption isotherms. The change in the thermodynamic Gibbs potential ($\Delta\Phi$) is negative for both Se(IV) and Te(IV), indicating that the sorption of both elements is selective on AMP. This is due mainly to the increase in the entropy of the system, since the enthalpy factor is unfavourable in this case ($\Delta H > 0$). The conditions for optimum sorption of selenium and tellurium coincide with the existence region[94–97] of the known double and triple complexes of Se(IV) and Te(IV) with molybdate and molybdophosphate: therefore, the concentrations of molybdenum and phosphorus in the equilibrium solutions were determined[42] during the measurement of the sorption isotherms under equilibrium conditions in order to clarify the interaction between these ions and the sorbent matrix. As the concentration of Te(IV) on the sorbent is increased, the amount of Mo(VI) and P(V) in solution is unchanged, but in the sorption of selenium it increases in proportion to the concentration of Se(IV), the average P : Mo ratio in solution being 1 : 12, i.e. the sorption of selenium is accompanied by a reconstruction of the sorbent matrix, leading to the transfer of molybdophosphate ions into the solution. Thus, published data on the mechanism of sorption lead to the conclusion that the sorption of ions of the second group on heteropoly acid salts is a multi-step process[42,43,98].

Step 1. Penetration of the sorbed ions into the macropores of the sorbent grain and ion exchange with a cation or acidic hydrogen of the sparingly soluble HPA salt.

Step 2. Sorption of the ions on the surface through interaction with the oxygen end-atoms of the anion structure, giving E–O–Mo bonds. This step is most marked when the sorbed ion has a strong tendency to form heteropoly acids. By comparing HPA stability data[69,99–102] with the conditions conducive to sorption of the corresponding ions[37–43,62,87–89,93,103] we arrive at the following affinity series:

$$Y^{III} < UO_2^{II} < Th^{IV} \simeq Ce^{IV} < Te^{IV} < Ti^{IV} < Zr^{IV} < Nb^{V}.$$

Step 3. In the case of ions with a high ionic potential the chemical interaction with the surface results in the removal of some of the molybdophosphate ions from the surface [as in the sorption of Se(IV)].

V. SORPTION OF IONS ABLE TO FORM THE COORDINATION SPHERE OF HETEROPOLY COMPOUNDS

Very little has been published on the sorption of molybdenum(VI), tungsten(VI), vanadium(V), and chromium(VI) ions on HPA series. However, we know[48] that these ions (in solutions) have a strong tendency to combine into polymeric structures, giving "mixed" heteropoly compounds. The best known of these are the mixed HPA of vanadium and molybdenum[104–107] and those of molybdenum and tungsten[108,109]. Some indirect information was obtained in studies of the coprecipitation of vanadium(V) with ammonium molybdophosphate[110,111]. The dependence of the extent of coprecipitation of vanadium on the amount of coprecipitant was found to vary with the concentration of vanadium in solution, i.e. to depend on the vanadium to phosphorus ratio. The incorporation of vanadium(V) into the precipitate is a maximum only when the conditions in the solution (acidity, excess of molybdate ions) are favourable to complex formation between phosphate, vanadate, and molybdate. Tsyganok and coworkers[111] have shown, by the molar ratio and isomolar series method, that a complex with a ratio of P : V = 1 : 1 is formed in solution during coprecipitation. Hence they concluded that the co-crystallisation process plays a dominant role in this system, since the replacement of one molybdenum atom by vanadium does not affect the structure of the heteropoly anion. The $PMo_{12}O_{40}^{3-}$ and $PMo_{11}VO_{40}^{4-}$ anions are isomorphous. The coprecipitation of vanadium on a pre-existing AMP precipitate has also been studied, and found to be less complete than coprecipitation during formation of the precipitate.

Thus, published data on the sorption mechanism of various ions on HPA salts lead us to conclude that more comprehensive studies of complex formation between the sorbed ions and the HPA anions are needed, under different conditions and in the presence of the components found in real mixtures, before the application of heteropoly acid salts in the separation and concentration of radioactive or stable isotopes can be further extended.

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The Mechanism of the Aromatisation of Paraffinic Hydrocarbons on Oxide Catalysts

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Data obtained in studies on the mechanism of the aromatisation of paraffinic hydrocarbons are examined. Attention is concentrated on studies carried out by isotope methods. It is shown that aromatic hydrocarbons are formed from paraffins on oxide catalysts via a single pathway—the successive dehydrogenation of the aliphatic hydrocarbon with formation of a six-membered ring (cyclodiene) as a result of the thermal cyclisation of a triene.
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I. INTRODUCTION

The aromatisation reaction was discovered independently in 1936 by three groups of Soviet chemists on catalysts of different kinds[1-4]. This reaction, which makes it possible to obtain comparatively simple aromatic compounds from paraffinic hydrocarbons, has naturally attracted the attention of investigators in all countries with a developed petroleum processing industry. The interest in the reaction was due not only to the likelihood of the creation of a new industrial process for the synthesis of aromatic raw materials but also to the possibility of determining the nature of the cyclising effect of the catalyst and the cyclisation mechanism by studying the reaction, i.e. due to the possibility of elucidating a series of new fundamental catalytic laws.

Numerous studies devoted to the aromatisation reaction have been published in Soviet and foreign literature, but its mechanism was elucidated only in the last decade. It was found that no special cyclising functions are required from aromatising oxide catalysts. In the available reviews[5-9] attention has been concentrated on the technological aspects of the process (the composition and properties of the catalysts, the methods for their treatment and modification, etc.), but the reaction mechanism proper has been considered relatively little; furthermore, in most instances it is treated erroneously from the standpoint of modern ideas[10-11].

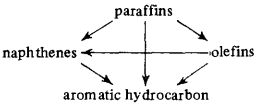
Although aliphatic hydrocarbons are aromatised on oxide catalysts in a fairly complex manner, the process can serve as a model reaction. Thus many characteristics of the aromatisation of paraffins established on oxide catalysts hold also for the platforming processes, the dehydrogenation of higher paraffins, etc.

The aim of the present review is to analyse the development and the present state of the ideas on the mechanism of the conversion of aliphatic hydrocarbons under aromatisation conditions on oxide catalysts mainly on the basis of the latest experimental data and information obtained with the aid of isotope research techniques.

II. THE MECHANISM OF THE AROMATISATION OF PARAFFINS ON OXIDE CATALYSTS

The first detailed discussion of the mechanism of the aromatisation reaction was held in 1939 at a session of the Faraday Society. A certain amount of experimental data had accumulated by that time, which permitted certain generalisations. It was established that aromatisation proceeds on chromium oxide and a number of other oxides in the temperature range 500–520 °C and on a platinum catalyst at a temperature 200° lower[12-17]. In the catalytic reaction mixtures obtained on oxides olefins were always present in addition to aromatic hydrocarbons[2-4,18], their content depending on the contact time[19]. The yield of aromatic products formed from olefins is higher than the yield obtained from the corresponding paraffins[20,21]. Paraffins and olefins without a straight six-carbon chain hardly form aromatic hydrocarbons.

Hoog et al.[21] proposed a scheme for the aromatisation reaction having included in the latter all the reaction pathways imaginable at the time. The scheme postulated the formation of olefins or cyclanes as intermediates:



(1)

According to the experimental data of Hoog et al.[21], the aromatisation of paraffins proceeds at least partially via a stage involving dehydrogenation to the corresponding olefins.

Consideration of thermodynamic data led to the conclusion[22] that the direct formation of benzene from hexane, by-passing any intermediates, i.e. the pathway leading to the conversion of paraffins into aromatic hydrocarbons in Scheme 1, is energetically the most favourable. From this standpoint (subsequently it was supported also by a series of other investigators), olefins are regarded as side products.

Pitkethly and Steiner[23] favoured two other mechanisms of the formation of aromatic hydrocarbons: via olefins as intermediates, by their cyclisation to a cycloparaffin and subsequent dehydrogenation of the latter to an aromatic hydrocarbon, or by the direct cyclisation of the paraffin to a naphthene via a stage involving a semihydrogenated state, which can also give rise to an olefin as a side product.

Both these mechanisms presuppose in one way or another the formation of a six-membered naphthene as an obligatory reaction stage. Probably at that time it was difficult to imagine the transformation of a paraffin into an aromatic hydrocarbon via a procedure other than the formation of a hexamethylene ring. Its further conversion into an aromatic hydrocarbon had been thoroughly investigated. It is noteworthy that the data of Pitkethly and Steiner with Hoog's correction[24] definitely indicated the intermediate formation of olefins, at least in the first reaction stage. Herington and Rideal[25] suggested that the first stage in the reaction is the obligatory cyclisation of the paraffin to a six-membered naphthene. They believe that the reaction is

possible only when at least one of the carbon atoms involved in cyclisation is located on the catalyst surface. Having calculated the probability of such cyclisation-promoting adsorption for different configurations of the hydrocarbon on the catalyst surface and having assumed that the degree of adsorption is proportional to the rate of reaction, the authors[25] found that these quantities agree with the experimental yields of aromatic hydrocarbons from the corresponding paraffins. They proposed the same mechanism also for the formation of aromatic hydrocarbons from olefins. However, this mechanism did not explain how *m*- and *p*-xylenes present in n-octane catalytic reaction mixtures are formed. In order to account for the origin of *m*- and *p*-xylenes (they cannot be obtained by the direct cyclisation of the paraffin to a six-membered naphthene), the authors[25] had to consider the formation of bicyclo-octanes of different structures, whose decomposition can give rise to the corresponding six-membered cyclanes.

At the same time studies in which olefins were detected among the reaction products continued to be published: the investigators discussed their role as intermediates[26-29]. As regards cyclohexane hydrocarbons, none of the investigators was able to detect them. This was explained by the fact that under aromatisation conditions the rate of dehydrogenation of cyclohexanes (according to the data of Kazanskii and Liberman[16]) greatly exceeds the rate of aromatisation of the corresponding paraffins. Komarevsky and Shand[30] attempted to detect *gem*-dimethylcyclohexane in the catalytic reaction mixtures obtained in the aromatisation of 2,2-dimethylhexane on an alumina–chromium oxide catalyst, assuming that it should not be dehydrogenated to an aromatic hydrocarbon. However, only *m*-xylene was found in the reaction products.

Nevertheless this result was insufficiently convincing to abandon the idea of the intermediate formation of cyclohexane in the aromatisation of paraffins[31-35], particularly since Kazanskii et al.[36] detected by Raman spectroscopy *gem*-dimethylcyclohexane in the catalytic reaction mixture obtained in the aromatisation of 3,3-dimethylhexane on platinised carbon, which indicated immediately the possibility of the direct cyclisation of the paraffin on a platinum catalyst. Comparison of the results of the studies of Komarevsky and Shand[30] with those of Kazanskii et al.[36] might have served as a basis for the hypothesis of significant differences between the mechanisms of the aromatisation of paraffins and oxide and metallic catalysts.

In subsequent years the attention of investigators was concentrated on oxide aromatisation catalysts, which appeared more promising at the time since new low-percentage alumina–platinum catalysts had not yet been introduced into practice. In Steiner's review[7], which deals exclusively with studies carried out on oxides, predominantly chromium oxide, catalysts, it is concluded that olefins must be formed as intermediates in the first stage of the aromatisation reaction on oxide catalysts.

However the kinetic evidence presented by Steiner[19,23,26,28,37] apparently proved to be insufficiently convincing to many other investigators and the latter continued to assume that olefins are formed as side products[31,35,38-41].

Inspection of the studies in the first stage of the research into the aromatisation reaction shows that mainly three possible reaction pathways were considered:

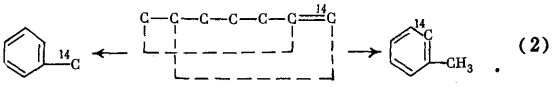
(1) the cyclisation of the paraffin to a six-membered naphthene in the first reaction stage followed by its dehydrogenation to an aromatic hydrocarbon;

(2) the formation of an olefin, which is subsequently converted into an aromatic hydrocarbon, also via a naphthene;

(3) direct transformation of the paraffin into an aromatic hydrocarbon on the catalyst surface.

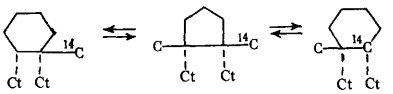
One should bear in mind that during the period when the above studies were carried out the methods for the analysis and separation of hydrocarbon mixtures were extremely complex and relatively uninformative. Studies involving a large number of analyses in the course of the experiment were therefore difficult. As soon as it became possible to use radioisotopes for the investigation of the mechanisms of chemical reactions, the latter were employed also in the investigation of the aromatisation of paraffins. These studies, involving the application of the method of tracer atoms[42], were begun as early as the 1950's and have continued up to the present time.

A study[43] of the transformation of [1-^{14}C]hept-1-ene over a chromium oxide catalyst revealed the presence of 50% of the radioactive label in the methyl group of the resulting toluene, which corresponds to the formation of aromatic hydrocarbons by the simple cyclisation of the aliphatic hydrocarbon via the mechanism



(2)

However only 26–29% of the label was found in the methyl group of toluene obtained[44] in the aromatisation of [1-^{14}C]heptane (depending on the degree of reaction). In order to account for these results, it was necessary to resort to more complex reaction mechanisms: with formation of a bicycloheptane (according to Herington and Rideal[25]) or with formation on the surface of the catalyst (Ct) of a cyclopentane-like adsorbed complex, which then isomerises to a six-membered cyclic compound and is subsequently dehydrogenated:



(3)

The formation of intermediate cyclopentanes was not confirmed experimentally[44].

In a study of the transformation of 2,2-dimethyl-4-[^{14}C]methylpentane, Cannings et al.[45] obtained *p*-xylene (yield 14%) and toluene (yield 3%) as the aromatisation products; the methyl groups of the xylene contained 50% of the label, while that of toluene contained 23–25% of the label. According to the authors, the reaction proceeds via a stage involving skeletal isomerisation with subsequent ring closure by the aliphatic molecule to give a six-membered cyclic compound.

The mechanism of the aromatisation reaction has been investigated in detail by the tracer atom method in studies by Pines and coworkers[46-60]. Three catalysts were used in studies during the period from 1959 to 1965:[46] chromium oxide (without a carrier), chromium oxide deposited on alumina with distinct acidic properties (type A), and chromium oxide deposited on alumina without pronounced acidic properties (type B). In the aromatisation of [1-^{14}C]-n-heptane it was observed[46-50] that the content of the label in the methyl group of toluene depends on the nature of the catalyst and varies during the experiment. In experiments with pure chromium oxide 44–47% of the radioactivity was detected in the methyl group of the toluene. In experiments with chromium oxide deposited on alumina the content of the label in the methyl group was 39 and 17% (for aluminas of types A and B respectively), increasing appreciably after several hours of the operation

of the catalyst. An analogous study has been carried out on the aromatisation of [1-^{14}C]-n-octane.

Since the results could not be explained on the basis of the known mechanisms, Pines suggested the intermediate formation of five-, seven-, and eight-membered rings, in addition to the six-membered rings, which then undergo isomerisation of the "contraction–expansion" type to give the six-membered rings. Pines and coworkers investigated the transformations of cyclanes—methylcyclopentane, substituted cyclohexanes[48], methylcycloheptane[47], and cyclo-octane[49], as well as paraffins for which these cyclanes might be aromatisation intermediates—and noted a similarity in the products of the aromatisation of paraffins and the corresponding cyclanes. The same analogy was noted in the distribution of the label in the hydrocarbon molecules when the products of the reactions of linear and the corresponding cyclic hydrocarbons were compared[49,51,59]. The authors regard this analogy as proof that the C_5, C_7, and C_8 cyclanes are intermediates in the aromatisation of the corresponding alkanes. They suggest that the size of the intermediate ring depends on the acidity of the catalyst. On chromium oxide and an acid catalyst of type A, five- and six-membered rings are formed preferentially, while on the "non-acid" catalyst of type B seven- and eight-membered rings predominate.

According to Pines' hypothesis, the distribution of the radioactive label in the aromatisation products should not depend on the position of the label in the initial paraffin, for example, in n-octane. Indeed, the site at which the contraction of the eight-membered ring begins involves any bond of the ring with equal probability. However, a comparative study of the aromatisation of [1-^{14}C]octane and [4-^{14}C]octane on a type B catalyst[48,49,51–53] showed that the distribution of the label in ethylbenzene and xylenes depends significantly on its position in the initial octane. Thus the content of the label in the aromatic rings of ethylbenzene and *o*-xylene obtained from [4-^{14}C]octane is from 92 to 97%, while the contents of the label in the same products obtained from [1-^{14}C]octane are respectively 68–50% and 39–8%.

Having considered next the possible distribution of the label under the conditions of the formation of an intermediate five-, six-, seven-, or eight-membered ring or even a bicyclic compound (according to Herington and Rideal[25]), Pines and coworkers concluded that the formation of only one of these intermediates cannot fully account for the experimental data. However, the combination of two or even three mechanisms involving the formation of intermediate rings of different structures can explain all the experimental results[51]. The studies by Pines have shown that the formation of cyclanes, including the six-membered cyclane, as aromatisation intermediates was not questioned in any way; other aromatisation pathways with participation of other intermediates were not in essence considered. Nor was the role of unsaturated hydrocarbons, particularly olefins, in the formation of aromatic hydrocarbons considered, although Pines and coworkers used gas–liquid chromatography for analysis and not only olefins but also dienes were detected in the catalytic aromatisation reaction products[49,51].

Thus the use of radioisotopes at this stage of the investigation helped little in elucidating the pathways leading to the transformation of paraffins under aromatisation conditions. This can probably be explained by the fact that the tracer atom method, which deals only with the location of the label in the starting materials and final reaction products, does not permit a conclusion concerning the nature of the intermediates. Experiment only indicated the location or transfer of the label to a particular position in the final product without any indication of the pathways leading to this transition.

In a study of the aromatisation of [4-^{14}C]heptane on catalysts of types A and B (in Pines' terminology), Feighan and Davis[61] observed that the bulk of the radioactive label is present in the $C_{(3)}$ position in toluene, but the $C_{(2)}$ and $C_{(1)}$ atoms as well as the carbon atom of the methyl group also proved to be radioactive. Comparison of the data obtained in a comparative study of the aromatisation of heptanes labelled in the 1- and 4-positions yielded a picture analogous to that obtained earlier by Pines for [1-^{14}C]- and [4-^{14}C]-octanes[62]. Feighan and Davis[61] suggested that, together with the direct cyclisation of heptane, there is also partial skeletal isomerisation of heptenes. The subsequent cyclisation of the iso-olefin can explain the transfer of the label from [4-^{14}C]heptane to the methyl group of toluene.

To demonstrate the direct cyclisation of the paraffin, Davis and coworkers[63,64] compared the products obtained on chromium oxide and alumina–platinum catalysts. Assuming that the possibility of the direct cyclisation on platinum has been demonstrated[36], the author claims that the difference which he nevertheless observed can be accounted for by the greater isomerising capacity of the chromium oxide catalyst compared with the platinum catalyst. For example, on the platinum catalyst Davis obtained toluene as the main product from *gem*-dimethylcyclohexane and 2,2-dimethylhexane. On the chromium oxide catalyst, toluene was also obtained from *gem*-dimethylcyclohexane, but 2,2-dimethylhexane gave rise to *m*- and *p*-xylenes and not the demethylated product. If the cyclohexane hydrocarbon had undergone isomerisation, the naphthene and paraffin aromatisation products would have been identical. Consequently Davis's results confirm the possibility of the skeletal isomerisation of the aliphatic molecule, but they do not demonstrate the existence of an intermediate naphthene. Thus in these studies too the role of unsaturated hydrocarbons was in essence not considered.

In a study of the formation of olefins from paraffins on the chromium oxide catalyst Timofeeva and coworkers[65–75] demonstrated with extensive experimental data that aromatic hydrocarbons are also always formed under these conditions. A small amount of olefins is then obtained from alkanes with a straight-chain structure, the amount of aromatic hydrocarbon being large, while isoalkanes (which are incapable of forming a six-membered ring without isomerisation) produced mainly olefins. Dienes were detected in the catalysts in both cases[70–72].

Studies[76–79] of the aromatisation of a series of paraffins and olefins ranging from C_6 to C_9 [77] on the alumina–chromium oxide–sodium oxide catalyst and of cyclanes ranging from C_5 to C_7 [78] and isoparaffins[79] also demonstrated, with a large number of examples, that the yield of aromatic hydrocarbons produced from olefins (particularly from alk-2-enes and alk-3-enes) is always greater than the yield obtained from paraffins. Furthermore, in the aromatisation of paraffins a sharp increment of the yield of aromatic hydrocarbons with increase of reaction temperature always follows the maximum content of olefins in the catalytic reaction mixture. On this basis, it has been concluded[76–79] that olefins play the role of intermediates in the aromatisation of paraffins. The above workers believe that the next stage of the reaction is cyclisation, preferentially the cyclisation of a C_6 olefin, since, according to their data, methylcyclopentane and methylcyclopentene give rise to very low yields of benzene under these conditions. However, Perrée and Blouri[77] did not detect either C_5 or C_6 hydrocarbons (other than

aromatic hydrocarbons) in the catalytic aromatisation reaction mixtures, but did find traces of dienes.

On the hypothesis that the rate of aromatisation must follow a first-order equation and that olefins must be formed as intermediates, Penchenkov and Zhorov[80-82] derived a kinetic equation for the two-stage reaction paraffins → olefins → aromatic hydrocarbons. Comparison of the experimental and calculated yields of heptane, octane, and nonane aromatisation products revealed a very great similarity[80,81]. It was observed that under these conditions the isomerisation of olefins with differing double bond positions proceeds faster than dehydrogenation[82]. Thus virtually an equilibrium mixture of isomeric olefins undergoes aromatisation and the olefin aromatisation reaction has been shown to be 7–8 times faster than the dehydrogenation of a paraffin.

Having used in the study of aromatisation mixtures of non-radioactiveheptane and heptanes with one of the carbon atoms replaced by the ^{14}C radioactive label, Lipovich and coworkers[83-86] showed definitely that heptenes are intermediates in the formation of toluene.

Thus the above group of studies again indicated the intermediate formation of olefins in the aromatisation of paraffins. However, subsequent olefin transformation pathways were virtually uninvestigated.

A new stage in the study of the mechanism of the aromatisation reaction became possible as a result of the application of a pulsed technique in combination with gas-chromatographic analytical methods. Rozengart et al.[87] investigated the composition of the heptene aromatisation products as a function of contact time on an alumina–chromium oxide–potassium oxide catalyst and observed that heptadienes were present in the catalytic reaction mixtures. It was found that, with increase of contact time, their contact passes through a maximum. For short contact times, the concentration of heptadienes is greater than that of toluene and the maximum heptadiene content occurs at the same time as the point of inflection in the S-shaped toluene curve. These data are fully consistent with the characteristics of consecutive reactions.

Since heptadienes can be regarded as intermediates, the authors[88-90] subsequently investigated kinetically the transformation of hepta-1,3-diene and observed that heptatrienes are present in the catalytic reaction mixtures. It was found that their content also passes through a maximum with increasing contact time, although the content of trienes is lower than that of toluene even for the shortest contact times. These results as well as data obtained in the study of the reactions of heptatriene and methylcyclohexadiene suggested[88] that the aromatisation of the paraffin proceeds via the successive dehydrogenation of the aliphatic molecule to trienes. Trienes readily undergo thermal cyclisation[91-93] with formation of cyclodienes, which are then dehydrogenated to the aromatic hydrocarbon: paraffin → olefin → diene → triene → alkylcyclohexadiene → aromatic hydrocarbon. In contrast to the previous schemes, this scheme does not postulate the intermediate formation of cyclohexane hydrocarbons.

It was necessary to test the reliability of this scheme by independent methods and to determine whether or not it constitutes the only pathway, the main pathway, or only one of many pathways to the transformation of alkanes into aromatic hydrocarbons.

The kinetic isotope method proposed by Neiman[94-97] and widely used in studies of the mechanisms of heterogeneous-catalytic reactions[42,98-113] was employed in subsequent investigations. In contrast to the tracer atom method, the kinetic isotope method is not concerned with the position of the label within the molecule, the molecule as a whole being treated as radioactive and the distribution of the label between the reaction products being estimated.

In order to determine whether or not cyclohexane hydrocarbons are intermediates in the aromatisation of a paraffin, for example, hexane, a study has been made[114] of the aromatisation on an alumina–chromium oxide–potassium oxide catalyst of mixtures of hexane and cyclohexane in which cyclohexane contained the radioactive label. If cyclohexanes were an intermediate in the reaction involving the conversion of hexane into benzene, one would expect a decrease of the molar radioactivity of cyclohexane in the catalytic reaction mixture relative to the initial value as a consequence of the formation of non-radioactive cyclohexane from n-hexane. This decrease should have been greater the lower the content of [^{14}C]cyclohexane in the initial mixture and the greater the degree of conversion of n-hexane. However, even in the case where the benzene content in the catalytic reaction mixture was many times greater than the cyclohexane content in the mixture, no decrease in the activity of cyclohexane was observed. Thus cyclohexane is not an intermediate in the aromatisation of n-hexane under the given conditions.

In order to elucidate the role of olefins, a study was made of the transformation of mixtures of n-hexane and hex-1-ene in which one of the components contained the radioactive label. In the aromatisation of non-radioactive hexane with added labelled hex-1-ene (with a molar radioactivity β) the benzene formed in the reaction was also radioactive (with a molar radioactivity γ). If hexene plays the role of an intermediate in this reaction, β should decrease in the course of the process (as a result of the formation of non-radioactive hexene from n-hexane), remaining, in conformity with the postulates of the kinetic isotope method[42], below the radioactivity of benzene:

$$\beta < \gamma. \qquad (4)$$

On the other hand, when the aromatisation of radioactive hexane mixed with unlabelled hexene is investigated, then the radioactivities of benzene and hexene should increase in the course of the reaction, but the increase should be such that the following condition is maintained:

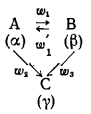
$$\beta > \gamma. \qquad (5)$$

The maintenance of this condition would suggest that hexene is indeed a precursor of benzene in the aromatisation of hexane. If other intermediates are formed during the reaction from the olefin, their molar radioactivities should have values intermedate between β and γ according to the postulates of the kinetic isotope method.

A study of the aromatisation of a mixture of hexane and [1-^{14}C]hexene showed[115] that the change in the radioactivities of hexenes and benzene during the reaction does indeed obey the rule indicated by inequality (4) (see Table). Thus, in contrast to cyclohexane, hexene is undoubtedly an intermediate in the aromatisation reaction. The tabulated data show that the radioactivity of hexadienes is intermediate between those of hexene and benzene. Consequently hexadienes are also obligatory intermediates in the aromatisation reaction.

Although it has been shown[114] that hexane does not undergo catalytic cyclisation in the first reaction stage, one cannot claim that cyclisation does not occur in the stages involving the formation of olefins or dienes. Furthermore, the results of the two studies quoted above do not rule out the possibility of the reaction on the surface of the catalyst without the liberation of intermediates into the reaction space—in the way imagined, for example, by Taylor and Turkevich[22].

An answer may be obtained to these questions by employing in the investigation the method involving the calculation and comparison of the reaction rates proposed by Balandin and coworkers[101–103]. Each multistage reaction can be represented by the triangular scheme



(6)

where A, B, and C are the initial reactant, the intermediate, and the final product respectively and α, β, and γ are their molar radioactivities. The reaction rates w_1, w_1', w_2, and w_3 via different pathways are calculated by the equations of the kinetic isotope method from the changes in the concentrations and molar radioactivities of the reaction components. The rate of accumulation of the final product $d[C]/dt$ is calculated wholly from the change in its concentration. It follows from Scheme (6) that, when $w_2 = 0$, the reaction is consecutive and involves the intermediate B; if $w_3 = 0$, then B is a side product; when $w_2 \neq 0$ and $w_3 \neq 0$, the reaction proceeds via the two pathways simultaneously.

Results of experiments on the aromatisation of the hexane–[^{14}C]hex-1-ene mixture (530 °C).[115]

Mixture components	Initial mixture	Content in catalytic reaction mixture, mole %					Molar radioactivity, %***					
		catalyst sample, mg					initial mixture	catalyst sample, mg				
		2.5	5.0	20.0	50.0	100.0		2.5	5.0	20.0	50.0	100.0
Cracking products*	—	0.6	2.0	1.9	5.2	6.1	—	—	—	—	—	—
n-Hexane*	59.0	59.0	58.0	56.0	47.8	45.7	—	—	—	—	—	—
Hexenes	41.0	34.0	30.3	13.7	4.6	3.1	100	102	101	90	71	10
Hexadienes**	—	3.2	5.1	11.1	5.2	2.2	—	100	97	92	73	18
Isohexadienes*	—	0.2	0.2	0.6	1.0	0.8	—	—	—	—	—	—
Benzene	—	2.2	4.2	16.7	36.2	42.1	—	99	97	95	80	77

*The radioactivity was not estimated quantitatively.

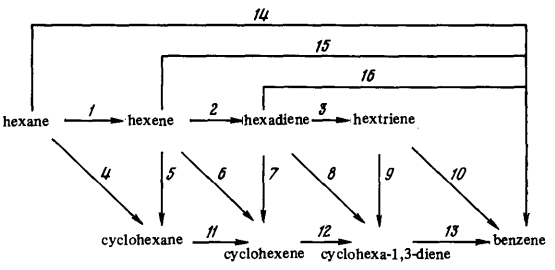
**The sum of all the isomers detected in the catalytic reaction mixture.

***The molar radioactivity of the products was calculated as a percentage relative to the molar radioactivity of the hexenes in the initial mixture.

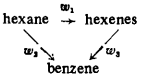
Evidently the reaction is in reality more complex than suggested by Scheme 6, because each stage also involves the adsorption and desorption of the reaction components on the surface of the catalyst. However, it is known[98–100] that the consecutive nature of the reaction, established with the aid of the kinetic isotope method, also implies that the desorption and adsorption of the reaction components are faster than the reaction itself.

We shall now consider the conversion of hexane into benzene from the standpoint of Scheme (6). Comparison of the literature data and the present author's results[114,115] makes it possible to set up a model of the hexane transformation reaction, which includes the three main aromatisation pathways (see Scheme A). Transformation via stages *1–3*, *9*, and *13* is consistent with the scheme proposed by Rozengart et al.[88] The cyclisation of hexane or of the successive intermediates corresponds to reactions *4–10*. Any other pathways leading to the transformation of hexane into benzene are included in pathways *14–16*.

Scheme A



The kinetic isotope method makes it possible to consider and investigate the pathways involved in the transformation of the reaction components at each stage. The first stage can then be represented as follows:



(7)

If $w_2 \neq 0$, the implication is that benzene can be formed from hexane not only via hexenes but also via some other pathway. Cyclohexane is ruled out as an intermediate[114], but there may be other intermediates which have not been detected in catalytic reaction mixtures for one reason or another. Furthermore, aromatisation can occur on the surface of the catalyst without the desorption of the intermediates into the reaction space. On the other hand, if hexane is converted into benzene via a single pathway, then evidently $w_2 = 0$ and w_3 and the rate of accumulation of benzene in the system $d[C]/dt$ should be equal.

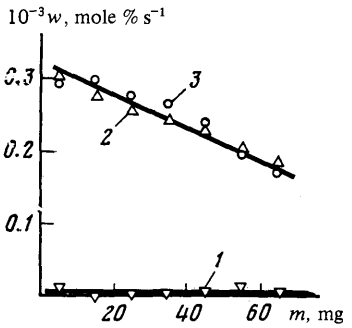
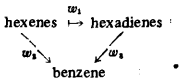


Figure 1. Variation of the rates of transformation of the components of the hexane–[^{14}C]hex-1-ene–benzene mixture with increasing contact time (catalyst sample):[117] *1)* w_2; *2)* dc/dt; *3)* w_3 [for the significance of the symbols, see Scheme (7)].

All these hypotheses have been tested[116,117] by investigating the aromatisation of the hexane–[^{14}C]hex-1-ene–benzene ternary system. The results of the calculation of the rates of reaction by the equations of the kinetic isotope method, in conformity with Scheme (6), from the experimental data of the above studies are presented in Fig.1. It was found that the rates of accumulation of benzene $\{d[C]/dt\}$ and of conversion of hexene into benzene (w_3) are the same within the limits of the accuracy of the calculation, while the rate w_2 of the transformation of hexane into

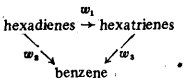
benzene by-passing hexene is virtually zero. Consequently there is no pathway other than that via hexene in the transformation of hexane into benzene and the possibility of reaction via pathway *14* is ruled out.

The same method was then used to investigate the transformations of hexenes and hexadienes:



(8)

It was found that only the dehydrogenation of hexenes to hexadienes takes place in the second stage of the reaction[118,119]. The results of the calculation of the rates in this system are illustrated in Fig.2. Furthermore, special experiments with [^{14}C]cyclohexane showed that there is no cyclisation of hexenes to cyclohexane or cyclohexene[119]. The transformations of hexadienes into hexatrienes† also proceed via a single pathway [see Scheme (9) and Fig.3]:[119]



(9)

There is no cyclisation at this stage, although the possibility of the direct transformation of hexadienes into cyclohexa-1,3-diene has been discussed in the literature as one of the probable cyclisation pathways[120].

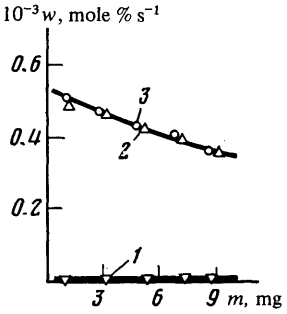


Figure 2. Variation of the rates of transformation of the components of the [^{14}C]hex-1-ene–hexadienes mixture with increasing contact time[119]: *1)* w_2; *2)* dc/dt; *3)* w_3 [see Scheme (8)].

Consequently pathways *5–8* and *15–16* (Scheme A), postulating the catalytic cyclisation or direct transformation of hexanes and hexadienes into benzene, do not occur.

An aliphatic molecule is dehydrogenated in the aromatisation reaction to the triene stage. Scheme A postulates two possible reaction pathways for the triene: thermal cyclisation to cyclohexa-1,3-diene with its subsequent dehydrogenation to benzene (pathways *9* and *13*) or direct transformation of the triene into benzene by-passing the cyclohexadiene formation stage *10*.

As was to be expected, hexatriene mixed with [^{14}C]hexadienes reacts wholly at 520 °C after very short contact times (Fig.4) [118] and is almost completely converted into cyclohexa-1,3-diene, the concentration curve of which has a distinct maximum. With increase of contact time, the concentrations of cyclodiene and benzene vary in opposition. The molar radioactivity of benzene is lower than that of cyclohexadienes and both increase with increasing contact time.

If the molar radioactivities of the hexadienes, cyclodienes, and benzene, are denoted by α, β, and γ respectively, then, taking into account the transformation of hexadienes into hexatrienes demonstrated above[119], one can set up the following sequence:

$$\alpha > \beta > \gamma.$$

This type of sequence for a mixture in which the first component is radioactive indicates, according to the kinetic isotope method, that the transformations of hydrocarbons investigated constitute a single chain: hexadiene → hexatriene → cyclohexa-1,3-diene → benzene. Returning now to Scheme A, one may conclude that the transformation proceeds via pathways *9* and *13*, while pathway *10* does not operate.

Thus, in considering the set of consecutive stages of the transformation of hexane into benzene, it is seen that, under the conditions of aromatisation on the alumina–chromium oxide–potassium oxide catalyst, neither hexane, nor hexene, nor hexadiene undergo catalytic cyclisation. Only the triene is converted into a cyclic product, but a catalyst is not required for this stage. All the remaining reactions constitute stages involving the dehydrogenation of the aliphatic molecule and then of cyclohexadiene. Presumably there are no pathways leading to the formation of the aromatic hydrocarbon on the chromium oxide catalyst other than those indicated below in Scheme (10).

hexane → hexenes → hexadienes → hexatriene → cyclohexa-1,3-diene → benzene. (10)

This scheme explains not only the obligatory presence of olefins and dienes in the catalytic reaction mixtures obtained on oxides but also the high yields of aromatic hydrocarbons from olefins. According to this scheme, hydrocarbons without a straight six-carbon chain can be aromatised only after passing through a skeletal isomerisation stage; consequently in this case one cannot expect high yields of aromatic compounds. It also becomes understandable why no investigators were able to detect cyclohexane hydrocarbons in the catalytic aromatisation reaction mixtures—they are not formed in this reaction.

The same scheme makes it possible to explain also the experimental data obtained in the study of the aromatisation of n-octane on the alumina–chromium oxide catalyst[121–128]. The question of the origin of *m*- and *p*-xylenes produced from n-octane is known to be the most complex in this instance. To account for their origin, the idea of the formation and isomerisation of cyclanes in the aromatisation process was in fact resorted to. However, the formation of isomeric xylenes can be readily understood if the aromatisation of n-octane is considered from the standpoint of the successive dehydrogenation scheme.

It has been shown that the isomerisation of aromatic C_8 hydrocarbons does not occur[46,47,53,121,122], so that the formation of structures leading to these xylenes takes place at intermediate stages of the reaction. If the formation of cyclanes constitutes this intermediate stage, then the ratio of *o*-xylene and ethylbenzene, on the one hand, and *m*- and *p*-xylenes, on the other, in the cyclane aromatisation products should be the same as in the aromatisation of n-octane. Furthermore, the content of *m*- and *p*-xylenes obtained in the aromatisation of 1,2-dimethylcyclohexane and ethylcyclohexane proved to be 3–100 smaller than in the aromatisation of n-octane[128]. Thus the isomerisation of

†Owing to the high reactivity of hexatriene, these experiments were performed at a temperature 100° lower than in the previous study.

the aliphatic intermediate actually accounts for the formation of *m*- and *p*-xylenes. The occurrence of this skeletal isomerisation of the aliphatic molecule under the conditions of the aromatisation on the chromium oxide catalyst is indeed confirmed by the presence of iso-octanes in the catalytic aromatisation reaction mixtures obtained from n-octane[121,122] and isohexadienes and in the catalytic reaction mixtures obtained from n-hexane[129], and it has been shown in the latter case that the skeletal isomerisation can be undergone not only by the unsaturated hydrocarbon but also by the alkane molecule. The increase of the yields of ethylbenzene and styrene with increasing temperature or degree of dilution of the reaction mixture by the inert carrier gas[125] can also be accounted for within the framework of this mechanism[88].

Subsequent studies showed that the kinetic picture observed in the aromatisation of n-hexane in the presence of molybdenum[139,140], vanadium[141], titanium[141], and tungsten[142] oxides deposited on alumina is fully consistent with the consecutive reaction and that the mechanism of aromatisation on these catalysts is the same as on the chromium oxide catalysts. Evidently the above scheme, involving the successive dehydrogenation of the aliphatic hydrocarbon, is applicable to the description of the aromatisation not only on chromium oxide but also on other oxide catalysts.

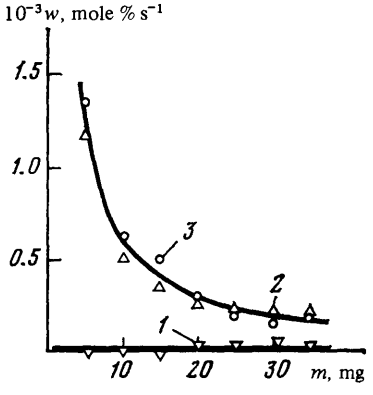


Figure 3. Variation of the rates of transformation of the components of the [^{14}C]hexadienes–hexatrienes mixtures with increasing contact time[119]: *1*) w_2; *2*) dc/dt; *3*) w_3 [see Scheme (9)].

It is noteworthy that in recent years studies have been published in which other aromatisation mechanisms have been put forward which in our view are not adequately supported. Thus, in studies[130,131] of the kinetics of aromatisation, the partial pressure of hexane in the system was varied by adding diluent gases (He, N_2, CH_4 and H_2) to a constant stream of hydrocarbon vapour. It was observed that the decrease of the partial pressure of hexane in a stream of helium, nitrogen, and methane hardly affects the yield of benzene, but reduces the yield of hexenes by a factor of 2. On the other hand, in a stream of hydrogen the yield of benzene decreases sharply, while the yield of hexenes increases somewhat. On the other hand, when the starting material is hexene, then the yield of benzene in a stream of helium, nitrogen, and methane increases with decrease of the partial pressure of hexene.

Being unable to account for these findings on the basis of Scheme (10), Shapchenko and Rudenko[130,131] therefore believe that the aromatisation of hexane on the alumina–chromium oxide–potassium oxide catalyst proceeds via a stage with formation of hexene, which is subsequently converted into a polymolecular complex on the catalyst surface[132,133]. The decomposition of this complex leads to benzene, cracking products, and coke formation. From our point of view, the anomalous results obtained in the above studies[132,133] can be simply explained. The independence of the yields of benzene of the partial pressure of hexane in a stream of helium, nitrogen, and methane observed in these investigations is only apparent, since in the experimental method employed the decrease of the partial pressure of hexane is accompanied by a decrease of contact time. Dilution of the system with a carrier gas (other conditions being equal) enriches the catalyst in benzene[134], while a decrease of contact time reduces its yield. The joint influence of these two factors can create the illusion that the yield of benzene is independent of the partial pressure of hexane.

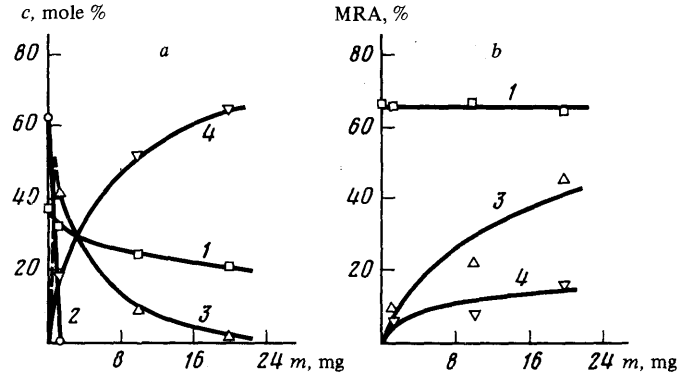


Figure 4. Variation of the concentration *c* (*a*) and the molar radioactivities (MRA) (% relative to the initial radioactivity) (*b*) of the products of the transformation of the [^{14}C]hexadienes–hexatrienes mixture at 530 °C as a function of contact time: *1*) hexadienes; *2*) hexatrienes; *3*) cyclohexa-1,3-diene; *4*) benzene[118].

As regards the influence of the hydrocarbon, which is manifested by an increase of the yield of olefins and a decrease of the yield of aromatic hydrocarbons, the above problem has already been considered and solved[127] in terms of mechanism (10).

Krzywicki and coworkers[135–137] detected cyclohexane and methylcyclohexane in the aromatisation of hexane and heptane on the comparatively little investigated alumina–chromium oxide–iron oxide catalyst[136,137]. The authors believe that these cyclic hydrocarbons are intermediates on the grounds that the curves representing their content in the catalytic reaction mixtures pass through a maximum as a function of time. However, it is difficult to regard this conclusion as sufficiently well founded because the kinetic picture presented by the authors is inconsistent with the kinetics of a consecutive reaction—the maxima are insufficiently distinct and the curve representing the content of the final product is not S-shaped.

Krzywicki et al.[135] did not detect dienes in the catalytic reaction mixtures obtained from paraffins and olefins, which is surprising because the formation of dienes had been detected earlier[138] on the same catalyst (up to 2%) but neither cyclanes nor cyclenes had been found. We therefore studied in greater detail[148] the transformations of hexane, hex-1-ene, and hexa-1,5-diene (on the catalyst prepared as described by Krzywicki and Malinowski[136]) mainly for short contact times. The kinetic picture obtained shows that hexenes and hexadienes are undoubtedly intermediates in the aromatisation of n-hexane on this catalyst.

In recent years studies on the aromatisation of paraffins on oxide catalysts have continued[143-147], but no new experimental facts have been observed which would necessitate a revision of the mechanism of this reaction presented above [Scheme (10)].

* * *

Thus analysis of the experimental data and in particular data obtained by the kinetic isotope method showed that the transformation of paraffins into aromatic hydrocarbons on the oxide catalysts investigated proceeds almost wholly via a single pathway—the successive dehydrogenation of the aliphatic molecule with formation of a six-membered ring by the thermal cyclisation of a triene. Only one function is required from the aromatisation catalyst, namely the ability to effect dehydrogenation.

Evidently this mechanism can be extended also to all other oxide catalysts used for the aromatisation of paraffins. However, the mechanism of the formation of the aromatic hydrocarbon on catalysts containing metals, including platinum group metals, is significantly more complex and therefore requires separate consideration.

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Perimidines

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The review deals with studies devoted to the methods of synthesis, physical and chemical properties, and the practical applications of perimidines—the first class of heteroaromatic compounds with distinct amphoteric chemical properties. i.e. the ability to react readily with both electrophiles and nucleophiles.
The bibliography includes 266 references.

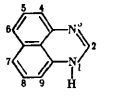
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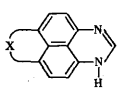
I. INTRODUCTION

Heteroaromatic systems are known to be very clearly divisible[1-3] into compounds with an excess of π electrons (e.g. pyrrole) and those with a deficiency of π electrons (e.g. pyridine). Electrophilic substitution and oxidation reactions are characteristic of the former, while the latter react mainly with nucleophiles, are difficult to oxidise, but are comparatively readily reduced. Studies in recent years apparently made it possible to discover for the first time a heteroaromatic system exhibiting simultaneously the distinct properties of compounds with an excess and deficiency of π electrons[4]. Such a system is perimidine (I), whose amphoteric chemical properties make it an interesting object of study. In view of the promising nature of such investigations and the increasing number of publications on the chemistry of perimidine, it has become necessary to survey them. The only review on perimidines was published in 1958 [5] when few data were available on their physical properties and reactivity; it therefore included only studies on the methods of their synthesis from 1,8-naphthylenediamines.

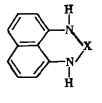
This review provides a compilation of the literature on the perimidine chemistry published up to June, 1980. It includes also data on the chemistry of aceperimidine (II), aceperimidylene (III), and hydrogenated compounds: 2,3-dihydroperimidine (IV) perimidone (V), and thioperimidone (VI).



(I)



(II) X = CH_2CH_2; (III) X = CH=CH



(IV) X = CH_2; (V) X = C=O; (VI) X = C=S.

Perimidine was first obtained and described in detail by Sachs[6] in 1909, while 2-methylperimidine had been described somewhat earlier[7,8]. Individual representatives of perimidines were apparently synthesised as early as the past century[9-11] by the interaction of 1,8-naphthylenediamine with a series of carboxylic acids and their derivatives. However, the compounds could not be obtained in a pure state and their structure could not be established. At the present time the name "perimidine" has been confirmed by IUPAC rules[12], but other names can also be encountered in the literature; 1*H*-naphtho-[1,8-*d*,*e*]pyrimidine, 1*H*-benzo[*d*,*e*]quinazoline, perinaphthimidazole, and 1*H*-1,3-diazaphenalene.

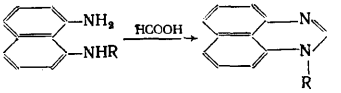
II. METHODS OF SYNTHESIS

The vast majority of the methods of synthesis of perimidines are based on the reaction of 1,8-naphthylenediamine (VIIa) (NDA) and its derivatives with various compounds containing a carbonyl group. The reaction with carboxylic acids and their derivatives makes it possible to obtain perimidines immediately, while the reaction with aldehydes and ketones leads to 2,3-dehydroperimidines. The latter can be usually readily converted into perimidines. The high reactivity of NDA can be accounted for by the powerful withdrawal of the unshared electron pairs of the two peri-amino-groups (the peri-interaction[13]). On cyclisation, this withdrawal ceases, which is accompanied by an energy gain.

1. Synthesis from 1,8-Naphthylenediamines

(a) Synthesis of Perimidines from NDA and Various Cyclising Agents

Carboxylic acids. This method yields especially satisfactory results when formic acid is used. Thus perimidine[6,14], 1-methylperimidine[15], 1-phenylperimidine[16], and 1-(2,4-dinitrophenyl)perimidine[17] (VIII) are formed in high yields when the diamines (VII) are refluxed with an excess of HCOOH:



(VII) (VIII)

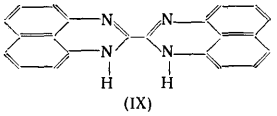
VII: (a) R = H, (b) R = CH_3, (c) R = C_6H_5, (d) R = 2,4-$(NO_2)_2C_6H_3$.

Aceperimidine[18], 1-methylaceperimidine[19], 6-chloroperimidine, 6-bromoperimidine[20], 6-hydroxyperimidine[21], 6-sulphoperimidine, 5,8-disulphoperimidine[22], and 6-phenylazoperimidine[23] have been obtained analogously from NDA derivatives substituted in the naphthalene ring.

The use of other acids does not always give rise to satisfactory results. Thus, when NDA is heated with trifluoroacetic acid[24], acetic acid, and α-, β-, and γ-amino-acids[25], the corresponding-substituted perimidine is formed at best in trace amounts. In order to increase the yield, it has been suggested that the mixture be refluxed in 4 *N* hydrochloric

acid[25-27]. Under these conditions, the interaction of NDA with glycolic, mandelic, thioglycolic[25], and lactic[26] acids leads to the formation of 2-hydroxymethyl-, 2-α-hydroxybenzyl-, 2-mercaptomethyl-, and 2-α-hydroxyethyl-perimidines. The first of these compounds can be obtained also in the absence of hydrochloric acid[6]. 2-R-Perimidines are obtained from high-molecular-weight aliphatic acids in low yields even in 4 *N* HCl.[27] On the other hand, when they are fused together with NDA, the products are salts of 2-R-perimidines, from which the free bases can be isolated on treatment with alkali[28] (in an earlier communication[29] it was erroneously stated that only *N,N'*-diacyl derivatives of NDA are formed in this reaction). The interaction of NDA with α-hydroxyphenylacetic acid results in the formation of 2-(α-hydroxybenzhydryl)perimidine[30].

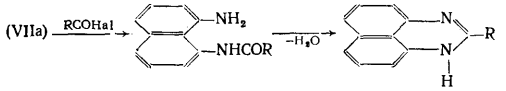
A satisfactory result of the reaction of NDA with aromatic acids has been reported[29,31,32]. When NDA was fused together with quinoline-α-carboxylic acid, 2-(α-quinolinyl)-perimidine was obtained[33]. The individual compounds could not be isolated in the reaction of NDA with pyruvic and phenylpyruvic acids[25].



(IX)

With the exception of oxalic and malonic acids, aliphatic dicarboxylic acids react with NDA to form ω-(2-perimidinyl)-alkanecarboxylic acids[27]. Oxalic acid[6,27] gives rise to a mixture of compound (I) and 2,2'-diperimidine (IX), which is a result of the decarboxylation and interaction with NDA of the intermediate perimidine-2-carboxylic acid respectively. The reaction of NDA with malonic acid produces a mixture of 2-methylperimidine and compound (V).[34]

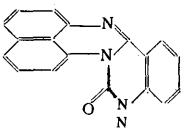
Hydrogen halides. This method is one of the best for the synthesis of 2-substituted perimidines (X). The reaction proceeds via the formation of the monoacyl derivative (XI). The formation of a certain amount of *N,N'*-diacyl derivatives of NDA, which, incidentally, can be readily separated from compounds (X) by virtue of their low solubility, can be regarded as the only disadvantage of the method.



(XI) (X)

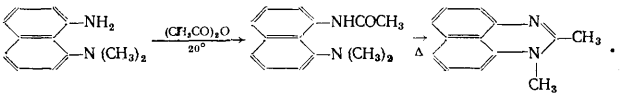
In particular, the following derivatives (X) have been obtained by this method; compounds with R = CH_3,[25,35] C_5H_{11}, C_6H_{13},[29] $C_{11}H_{23}$,[25,36] $C_6H_5CH_2$,[6] C_6H_5,[6,25] 4-$CH_3OC_6H_4$,[29,32] 2-, 3-, and 4-$O_2NC_6H_4$, C_6H_5=CH, CH_3CH=CH,[32] CH_2Cl,[37] CH_2F, CHF_2,[166] perfluoroalkyl, C_6F_5,[24,38] 3- and 4-$CF_3C_6H_4$, $CF_3OC_6H_4$, and $CF_3SC_6H_4$.[39] The method is suitable for the synthesis of 1,2-disubstituted perimidines[24,38,166] and also compounds such as 1,4-bis(2-perimidinyl)benzene and 1,5-bis(2-perimidinyl)naphthalene[35]. The only diamine which could not be converted into the corresponding perimidine on treatment with acid chlorides (and anhydrides) proved to be compound (VIId).[17]

The reaction of NDA with oxalyl chloride[40] leads to the formation of compound (IX) in 95% yield. The symmetrical *N*-substituted[41] and *C*-substituted derivatives (IX) [40] can be obtained similarly. The reaction of NDA with 2-isocyanobenzoyl chloride results in the formation of a derivative of quinazolinoperimidine (XII):[42]



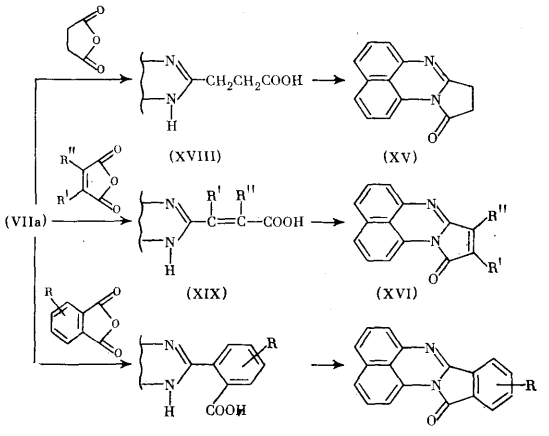
(XII)

Acid anhydrides. Heating NDA with acetic[8,25] and trifluoroacetic[24] anhydrides constitutes the best method of synthesising 2-methyl- and 2-trifluoromethyl-perimidines. The following derivatives (X) have been obtained by this method from NDA and the anhydrides of the corresponding acids: compounds with R = C_2H_5,[6,43] iso-C_3H_7, n-C_4H_9,[32] C_6H_5,[44] and 2-$HO_3SC_6H_4$.[45] The method has been used successfully to synthesise 2-R-aceperimidines[46] and 1,2-disubstituted perimidines[24]. It is of interest that, when 1-amino-8-dimethylaminonaphthalene is refluxed with acetic anhydride, 1,2-dimethylperimidine (XIII) is formed, i.e. the process is accompanied by the elimination of the *N*-methyl group[15]. At room temperature the reaction stops at the stage involving the formation of compound (XIV):



(XIV) (XIII)

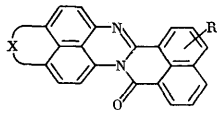
Compounds (XV)–(XVII), which Sachs called perinones, have been obtained by the reaction of NDA with the anhydrides of succinic[6], maleic[6,47,48], and phthalic[6,21,49] acids. The intermediate acids (XVIII)–(XX) can also be isolated:



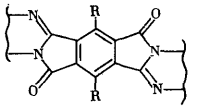
(XVIII) (XV) (XIX) (XVI) (XX) (XVII)

The synthesis of tetrafluorophthaloperinone by the reaction of NDA with tetrafluorophthalic anhydride has been described. 2-Tetrafluorophenylperimidine is then formed as a side product [as a result of the decarboxylation of an acid of type (XX) [38]]. When NDA [6,50,51] or 5,6-diaminoacenaphthene[18] is heated with naphthalic anhydride and its substituted derivatives, the products are naphthaloperinones (XXI). The reaction of NDA with the dianhydride of pyromellitic acid and its derivatives leads to perinones of type (XXII) [52] [isomers

of compound (XXII) with the *cis*-disposition of the C=O groups are also formed]:



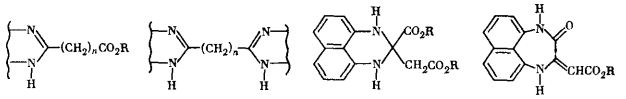
(XXI) R = H, NH_2 or NO_2; X = H_2 or CH_2CH_2



(XXII) R = H, Cl, Br or NH_2.

When NDA interacts with acid anhydrides, *N*,*N'*-diacyl-1,8-naphthalenediamines are also formed in a small amount[24,25,38].

Esters and iminoesters. Perimidines can be relatively readily obtained by treating NDA with carboxylic acid esters. Thus the reaction of NDA with ethyl carbonate leads to 2-ethoxyperimidine in a quantitative yield[53]. 2-Cyanomethylperimidine has been obtained by treating NDA with isobutyl cyanoacetate[54]. The reaction of NDA with dicarboxylic acid esters has been investigated[27]. If the reactants are taken in proportions of 1 : 1, the main product is the ester (XXIII). In the presence of a twofold excess of NDA, the diperimidines (XXIV) are formed in a low yield:

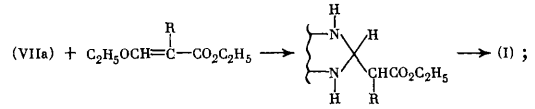


(XXIII) *n* = 0,1 (XXIV) *n* = 0-2 (XXV) (XXVI)

R = CH_3 or C_2H_5.

It has been reported[55,56] that the reaction of NDA with acetylenedicarboxylate esters leads to the formation of dihydroperimidines (XXV) together with diazepins of type (XXVI); the structure of the latter has not been rigorously demonstrated.

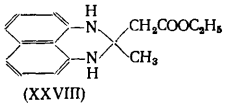
The interaction of NDA with ethoxymethylenemalonic or ethoxymethylenecyanoacetic ester[57] leads to the formation of compound (I). It is believed that cyclisation takes place at the carbon atom to which the ethoxy-group is linked and that the intermediate dihydroperimidine (XXV) splits off a molecule of $RCH_2CO_2C_2H_5$ and is converted into compound (I):



(VIIa) + $C_2H_5OCH{=}C(R){-}CO_2C_2H_5$ → (XXVII) → (I);

R = $CO_2C_2H_5$ or CN.

The interaction of NDA with acetoacetic ester is of interest. When the two reactants are refluxed without a solvent, 2-acetonylperimidine (X, R = CH_2COCH_3) is formed[6,25]. However, at room temperature the keto-group of acetoacetic ester is involved in cyclisation and the main reaction product is dihydroperimidine (XXVIII).[6] On heating, the latter loses a molecule of ethyl acetate and is converted into 2-methylperimidine:

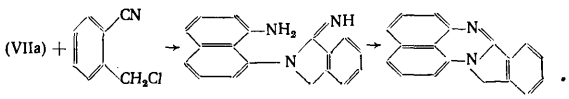


(XXVIII)

A convenient method of synthesising 2-substituted perimidines, particularly those containing complex and labile groups in the 2-position, involves the interaction of NDA with iminoesters. In particular, the following derivatives (X) have been obtained by this procedure: compounds with R = $CH_2CO_2C_2H_5$,[58] $CH(OC_2H_5)_2$, CH = NOH, CH_2CH_2NHR', *N*-oxo-2-pyridyl, and *N*-oxo-4-pyridyl.[59]

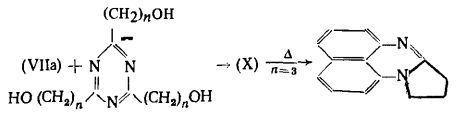
Acid amides and nitriles. There are few data concerning the synthesis of perimidine by the interaction of NDA with carboxylic acid amides and nitriles. Thus, when NDA is heated with caprolactam in the presence of inorganic acids, 2-(ω-aminopentyl)perimidine is formed[60,61]. In the interaction of NDA with ethyl oxamate the cyclisation involves both the ester and amide functional groups, as a result of which a mixture of the amide and the ethyl ester of perimidine-2-carboxylic acid is obtained[25].

At a high temperature acetonitrile and butyronitrile react with NDA dihydrochloride to form 2-methyl- and 2-n-propylperimidines[62]. The following reaction, leading to the perimidine (XXIX), is of interest[63]:



(VIIa) + → (XXIX)

Amidines. The interaction of NDA with formamidine[64] and diphenylformamidine[14] leads to the formation of compound (I). Cyclisation takes place also when NDA is heated with *sym*-triazines, which can be regarded as a kind of cyclic amidines. Thus 2,4,6-tri(ω-hydroxyalkyl)-1,3,5-triazines react with NDA at 220–230 °C to form compound [X, R = $(CH_2)_nOH$];[65] with *n* = 3, this compound cyclises at 250 °C to form the perimidine (XXX):

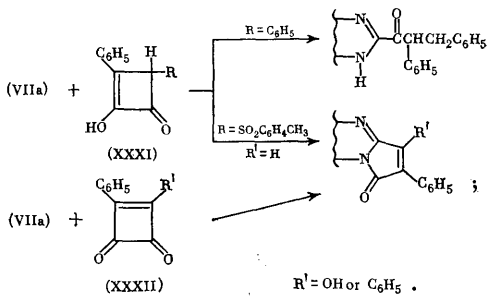


(VIIa) + → (X) $\xrightarrow[n=3]{\Delta}$ (XXX)

When NDA was heated with 2,4,6-tricyclopropyl-1,3,5-triazine, 2-cyclopropylperimidine was obtained[66]. Triazine itself gives rise to compound (I) in this reaction[67].

Other cyclising agents. 2-Aryl- and 2-heteroaryl-perimidines (X, R = C_6H_5, 4-iso-$C_3H_7C_6H_4$, 4-$CH_3OC_6H_4$, or 2-thienyl) have been obtained by the reaction of NDA with *N*-ethoxycarbonylthioamides[68]. The reaction of NDA with cyanobenzylideneanilines ArN = $C(CN)C_6H_5$ leads to 2-phenylperimidine[69]. 2-Acylindan-1,3-diones, 2-acyl-3-benzofuranones, etc. are effective cyclising agents which give rise to the perimidines (X, R = alkyl or aryl) on interaction with NDA.[70–72] It is of interest to note that these compounds react with *o*-phenylenediamine without the dissociation of the acyl–carbon bond, forming benzodiazepin derivatives.

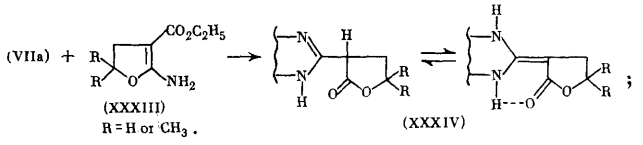
Reid and coworkers[47,48,73] investigated the reaction of NDA with derivatives of cyclobutenone (XXI) and cyclobutenedione (XXXII). Depending on the nature of the substituent R, the reaction leads to the formation of 2-acylperimidines or perinones:



(VIIa) + (XXXI) R = C_6H_5; R = $SO_2C_6H_4CH_3$, R' = H

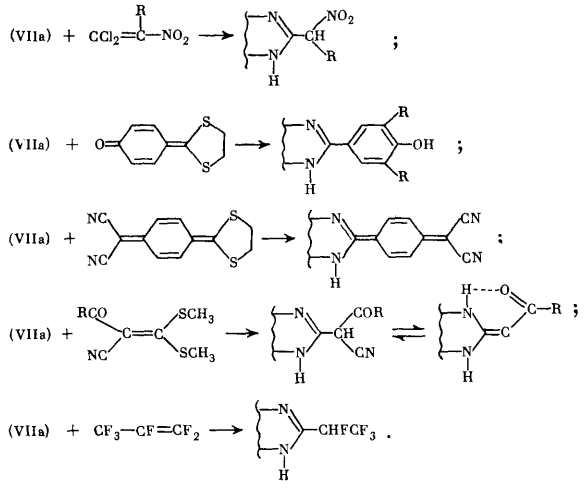
(VIIa) + (XXXII) R' = OH or C_6H_5.

The interaction of NDA with ethyl 2-amino-4,5-dihydrofuran-3-carboxylate (XXXIII) results in the formation of the perimidine (XXXIV), which exists predominantly in the tautomeric form (XXXIVb).[74] It is believed that the site of the μ-carbon atom in compound (XXXIV) is occupied by the carbon atom to which the amino-group is linked in compound (XXXIII), i.e. the reaction involves the recyclisation of compound (XXXIII):



(XXXIII) R = H or CH_3. (XXXIV)

The schemes below show that there is a possibility of the cyclisation of NDA to perimidines with the aid of activated unsaturated compounds: nitroethylenes[75], quinone derivatives[76,77], 1-acyl-1-cyano-2,2-dimethylmercaptoethylenes[78], and hexafluoropropene[79]:



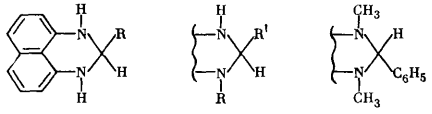
(b) The Synthesis of 2-Amino-, 2-Hydroxy-, and 2-Mercapto-Perimidines

2-Aminoperimidine (X, R = NH_2) is obtained in a high yield by the reaction of NDA with bromocyanogen[80,81] or cyanamide[82]. When NDA is fused together with ammonium thiocyanate[53] or thiourea[16], compound (X, R = NH_2) is formed in a mixture with thioperimidone (VI). The reaction of NDA with *S*-methylisothiourea derivatives leads to perimidine-2-carbamates (X, R = NHCOOR').[83,84] The synthesis of 2-arylamino-[53,85] and 2-dimethylamino-perimidines[86] by the reaction of NDA with aryl isothiocyanates and trichloromethyldimethylamine respectively has been reported.

2-Mercaptoperimidines (which exist in the thione form) are obtained by the reaction of naphthylenediamines with carbon disulphide. Thus compound (VI),[53] 2-mercapto-4,7-dimethylperimidine[87], and 2-mercaptoaceperimidine[18] have been synthesised in this way. It is possible to use potassium xanthate instead of CS_2.[53] Potassium cyanate, carbonate and chlorocarbonate esters[53], phosgene[17,53], and urea[88] are used as cyclising agents for the synthesis of perimidone (V) and its derivatives from NDA; almost all the methods yield satisfactory results. Aceperimidone is obtained similarly[89].

(c) Synthesis of 2,3-Dihydroperimidines from NDA and Aldehydes or Ketones

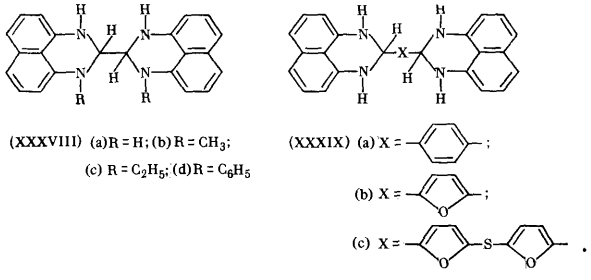
Aldehydes. Aldehydes interact with NDA in alcohol or benzene with formation of 2,3-dihydroperimidines (XXXV), where R = H, CH_3, CCl_3,[90,91] C_2H_5, n-C_3H_7, iso-C_6H_{13},[92] C_6H_5 [93-95], different halogeno-groups[93,94,96], hydroxy-group,[92-95] methoxy group,[92,94-96] 3,4-methylenedioxy-group,[92] dialkylamino-groups,[15,94] nitrophenyl,[93,94,97] 4-biphenylyl,[94] α-naphthyl,[96] ferrocenyl,[98] 1-propenyl,[95] β-styryl,[95] diethoxymethyl,[92] 2- and 3-pyridyl,[93,97] 2-quinolinyl, 2-pyrrolyl, 3-indolyl, 1-methyl-2-imidazolyl, 1-methyl-2-benzimidazolyl[93], 2-thienyl,[93,96] 2-furyl,[95,96,99] 5-methyl, 5-halogeno-groups, and 5-nitro-2-furyl.[93,99] 2-R-2,3-Dihydroaceperimidines are obtained similarly[100]. The reaction proceeds as a rule with a high yield and terminates after 2 to 3 h even at room temperature.



(XXXV) (XXXVI) (XXXVII)

R = CH_3 or C_6H_5; R' = H, Ar, or 2-furyl.

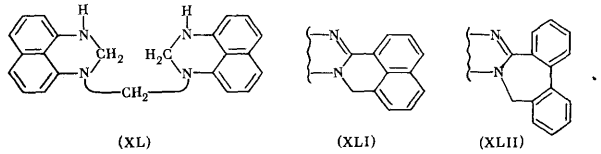
N-Methyl-[97] and *N*-phenyl-substituted[15,90] NDA (VII, b and c) also react with aldehydes to form dihydroperimidines (XXXVI), the reaction involving the amine (VIIc) proceeding with greater difficulty. *N,N'*-Dimethyl-1,8-naphthylenediamine interacts with benzaldehyde, forming compound (XXXVII).[15] The reaction of NDA [90] and its *N*-substituted derivatives[101] with glyoxal leads to hydrogenated bisperimidines (XXXVIII). Compounds (XXXIX) have been obtained analogously from aromatic dialdehydes[97].



(XXXVIII) (a) R = H; (b) R = CH_3; (c) R = C_2H_5; (d) R = C_6H_5

(XXXIX) (a) X = ; (b) X = ; (c) X = .

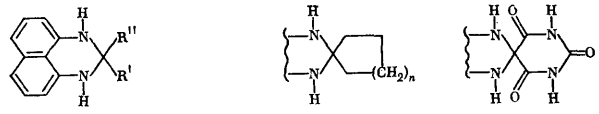
In a number of instances NDA reacts with aldehydes to form non-standard products. For example, the methane derivative (XL) is obtained together with compound (IV) if equimolar proportions of NDA and formaldehyde are used[90]. The reaction of NDA with phthalaldehyde, naphthalene-1,8-dialdehyde, and biphenyl-2,2'-dialdehyde results in the formation of the aromatised perimidines (XXXIX), (XLI), and (XLII) respectively[102].



(XL) (XLI) (XLII)

Ketones. Ketones interact with NDA to form 2,2-disubstituted 2,3-dihydroperimidines. Thus the reactions with acetone[8,103] and acetophenone[6] yield compounds (XLIII, a and b) respectively, while the reactions with cyclopentanone and cyclohexanone give rise to compounds (XLIV, a and b).[95]

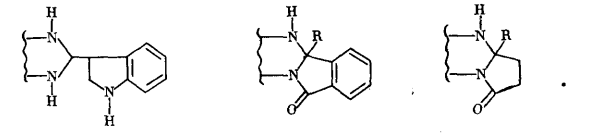
Acetone reacts as readily with NDA derivatives: 2-chloro-,[104] 4-sulpho-,[105] 3,6-dinitro-,[106] and 2,4,5,6-tetranitro-.[107] A method of synthesis of compound (XLIIIa) by the reduction of 1,8-dinitronaphthalene in the presence of the corresponding ketones has been proposed[108]. The reaction of NDA with alloxan and isatin[53] involves the ketone and not the amide carbonyl with formation of compounds (XLV) and (XLVI). The keto-group is also more reactive than the carboxy-group in the reaction of NDA with ω- and *o*-acyl derivatives of propionic and benzoic acids, as a result of which compounds of type (XLVII) and (XLVIII) are produced[109].



(XLIII) (a) $R^I = R^{II} = CH_3$; (b) $R^I = CH_3$, $R^{II} = C_6H_5$; (c) $R^I = CH_3$, $R^{II} = CH_3CO$

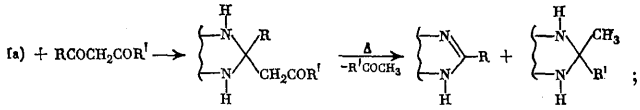
(XLIV) (a) $n = 1$; (b) $n = 2$

(XLV)



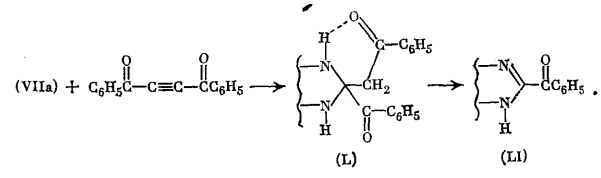
(XLVI) (XLVII) (XLVIII)

The interaction of NDA with diketones has been studied. Diacetyl yields dihydroperimidine (XLIIIc).[53] In the reactions with 1,3-diketones compounds of type (XLIX) are formed initially and are then aromatised on heating with elimination of the $R'COCH_3$ molecule and the formation of a 2-R-perimidine and a 2,2-disubstituted dihydroperimidine (as a result of the interaction of NAD with the eliminated ketone $R'COCH_3$).[53,110] For benzoylacetone, as an example, which gives rise to compound (XLIXb), it is seen that the aliphatic keto-group reacts with NDA more readily than the aromatic group:



(XLIX) (a) $R = R^I = CH_3$; (b) $R = CH_3$, $R^I = C_6H_5$; (c) $R = R^I = C_6H_5$.

The interaction of NDA with dibenzoylacetylene[111] takes place via one of the carbon atoms of the acetylenic bond. The dihydroperimidine (L) formed readily loses an acetophenone molecule on heating and is converted into 2-benzoylperimidine (LI):

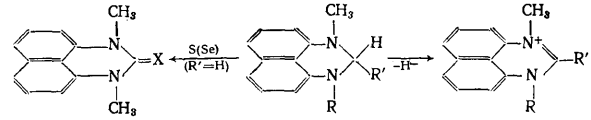


(L) (LI)

Under fairly severe conditions, such aromatisation takes place also for simple 2,2-disubstituted derivatives of 2,3-dihydroperimidine. For example, when a mixture of NDA and benzyl methyl ketone is heated at 315 °C, 2-methylperimidine is formed[112]. The reaction of NDA with diphenyltriketone [1,3-diphenyl-1,2,3-propanetrione] involves the central carbonyl and leads to 2,2-dibenzoyl-2,3-dihydroperimidine[110].

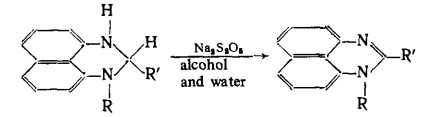
2. Synthesis of Perimidines from 2,3-Dihydroperimidines

The simplicity of the synthesis of 2,3-dihydroperimidines (DHP) and the availability of convenient methods for their dehydrogenation have recently made the reaction of NDA with aldehydes also one of the best methods of synthesising perimidines themselves. A whole series of reagents have been proposed for the aromatisation of DHP, whose choice in a specific instance depends on the nature of the substituents in the dihydroperimidine nucleus. For example, 1,3-disubstituted DHP (LII) are converted into perimidinium salts (LIII) by treatment with iodine[113], trityl perchlorate[114], and 1,3,5-trinitrobenzene[115]. The dehydrogenation of compounds (LII) and their aceperimidine analogues (with $R' = H$) by means of sulphur or selenium leads to the thiones (LIV) or selenones (LV):[113]



(LIV) X = S; (LV) X = Se. (LII) (LIII)

In the dehydrogenation of DHP with unsubstituted NH groups it is best to use sodium pyrosulphite $Na_2S_2O_5$.[97] The reaction is exceptionally clean, has a high yield, and is suitable for the synthesis of many 1- and 2-substituted perimidines (LVI), including those with substituents such as polyhydroxyalkyl groups:



(LVII) (LVI)

R, R′ = H, alkyl, heteroaryl, etc.

A single-stage synthesis of 2-R-perimidines from NDA and bisulphite adducts of aldehydes is also possible, but it has been achieved only for 2-phenylperimidine[116].

In those relatively few instances where the dehydrogenation with pyrosulphite is unsuccessful (1,2-diaryl- and 2-nitrophenyl derivatives of DHP),[97] it is possible to use palladium on carbon[25,92,98,99], manganese dioxide[117], or sulphur[118]. However, compounds with a nitro-group in the 2-aryl substituent are poorly dehydrogenated also by other dehydrogenating agents[93,97]. The aromatisation of the DHP is significantly hindered also in the presence of the *N*-phenyl [97,115] and *N*-acyl groups[114].

1,2-Disubstituted DHP (LVII) have been successfully aromatised by chloranil[117]. In the case of 2,3-dihydroaceperimidines chloranil dehydrogenates also the CH_2-CH_2 bridge, which results in the formation of aceperimidylenes[119].

The aromatisation of compounds (LVII) can also proceed with elimination of the groups R′ rather than the hydride ion. This is usually promoted by thermolytic conditions or by heating in acetic acid[93,101]. Examples of such aromatisation, in which the $RCRCH_2$ group was eliminated, have already been given above. Similarly, on heating in xylene and particularly in CH_3COOH, heteroaromatic substituents containing a heteroatom of the pyrrole type (pyrrolyl, 3-indolyl, 2-benzimidazolyl, etc.) are readily eliminated from the 2-position in compound (LVII).[93,101] Hydrogenated bisperimidines (XXXVIII) dissociate with rupture of the C–C bond and the formation of perimidines even on dissolution in chloroform[99,101]. This process takes place particularly readily for *N*-alkyl derivatives (XXXVIII, b and c).[101] However, the majority of 2-substituted DHP are resistant to thermolysis[93,

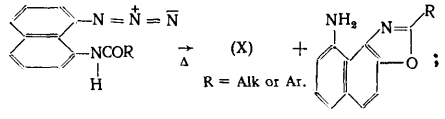
[101]. On the other hand, the thermolysis of 2-(2-pyridyl)- and 2-(2-quinolinyl-2,3-dihydroperimidines leads to the abstraction of a hydride ion and the formation of a 2-(2-pyridyl)- and 2-(2-quinolinyl)perimidines[93,101]. We may note that DHP containing β- and γ-pyridyl and quinolinyl groups in the 2-position are not aromatised in this way; the reason for this is not entirely clear.

The conversion of *N*-acetylated 2,3-dihydroperimidines into 2-methylperimidine under the influence of hydrochloric acid has been described but unfortunately has been little investigated[120].

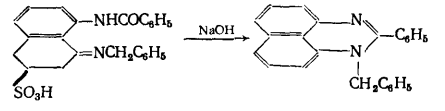
On the whole, DHP exhibit a lower hydride mobility and a greater stability than, for example, benzimidazolines[115], but after prolonged storage DHP gradually darken and decompose.

3. Other Methods of Synthesis of Permidines

In a number of studies perimidines have been synthesised not from NDA but from other 1,8-disubstituted naphthalenes. Thus, the reduction of 1-acetamido-7-hydroxy-8-nitroso-naphthalene[121] and 1-acetamido-5-hydroxy-8-phenylazo-naphthalene[122] yielded 4(9)-hydroxy- and 6(7)-hydroxy-2-methylperimidines respectively. The possibility of obtaining the *N*-oxide of 2-methylperimidine by the electrochemical reduction of 1-acetamido-8-nitronaphthalene has been reported[123]. Heating of 1-acylamino-8-azidonaphthalenes in trichlorobenzene leads to the formation of a mixture of 2-substituted perimidines and naphthoxazoles in a relatively low yield[124]:

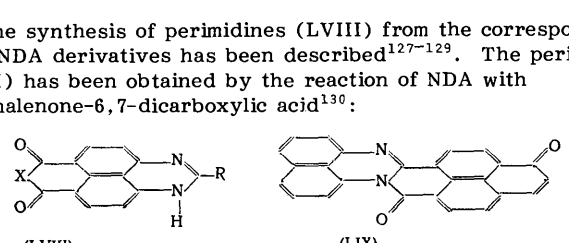


The reaction of the phthaloyl derivative of 1-amino-8-azidonaphthalene gives rise to phthaloperinone. On treatment with iron nonacarbonyl, 1,8-diazidonaphthalene is converted into perimidone in 6% yield[125]. When 8-benzamido-1-benzylimino-1,2,3,4-tetrahydronaphthalene-3-sulphonic acid was heated with alkali, 1-benzyl-2-phenylperimidine was obtained; another product of this reaction was 8-benzimido-1-naphthol[126]:

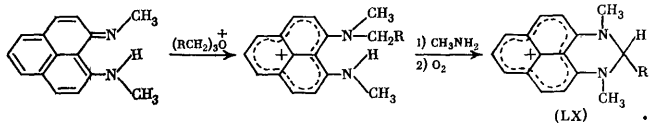


4. Different Condensed Systems Based on Perimidine

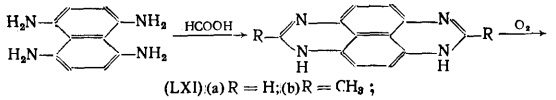
The synthesis of perimidines (LVIII) from the corresponding NDA derivatives has been described[127–129]. The perinone (LIX) has been obtained by the reaction of NDA with phenalenone-6,7-dicarboxylic acid[130]:



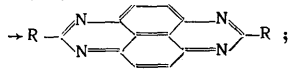
The dihydroperimidine (LX), in which the heteroring is condensed with a phenalenium ion, has been recently synthesised in accordance with the above scheme[131]:



On heating with formic acid, 1,4,5,8-tetra-aminonaphthalene gives rise to the red diperimidine (LXIa), which is extremely readily oxidised by atmospheric oxygen to a slightly greenish tetra-azapyrene (LXIIa).[132,133] The dimethyl derivative (LXIb), obtained by the reaction of 6,7-diamino-2-methylperimidine with acetic anhydride, behaves analogously[134]:

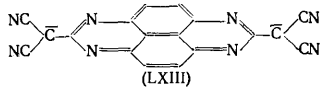


(LXI) (a) R = H; (b) R = CH_3 ;

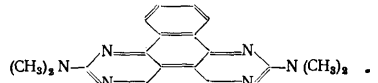


(LXII) (a) R = H; (b) R = CH_3 .

There are also data on the synthesis of tetra-azapyrene derivatives (LXIII) [135] and (LXIV).[136]



(LXIII)



(LXIV)

Polynaphthoperinone has been obtained by the reaction of tetramine with naphthalene-1,4,5,8-tetracarboxylic acid[137].

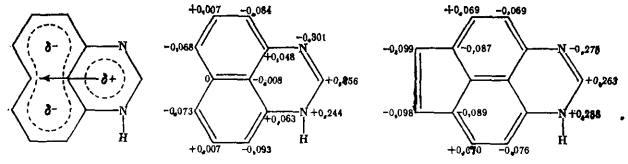
III. PHYSICAL PROPERTIES

1. Quantum-Mechanical Calculations and Aromaticity

The perimidine molecule is a 14π-electron system, but one of its electrons is not delocalised, which leads to a decrease of aromaticity. Thus the resonance energy per π electron (the REPE index) of perimidine is significantly lower than that of naphthoimidazoles[119]. Another feature of the π-electron structure of the molecule of compound (I) is the formal excess of π electrons in its heteroring in which there are seven π electrons. The expulsion of the "superfluous" super-Hückel electron from the heteroring to the naphthalene fragment of the molecule leads to the polarisation of the π-electron cloud corresponding to structure (LXV).[2] Such a shift has been confirmed by quantum-mechanical calculations [see diagram (LXVI)] regardless of whether one uses the simple Hückel method[138,139], the Pariser–Parr–Pople method[140], or the CNDO/2 method[141,142].

The distribution of electron density in the molecule of compound (I) is so non-uniform that it can be represented as consisting of, as it were, two parts: the μ-carbon atom with an unusually high positive charge and the negatively charged 1,8-naphthylenediamine residue. The transfer of π-electron density from the hetero-ring to the naphthalene system also takes place in naphthoimidazoles[3,139,142], but it is much weaker there. The maximum negative charge in compound (I) is concentrated in the 4- and 9-positions (the *ortho*-positions relative to the heteroring) and in the 6- and 7-positions (*para*-positions), while in the 5- and 8-positions

(*meta*-positions) it is virtually zero. Such alternation of charges can be explained by the alternant nature of the molecule of compound (I). The charge distribution is also very non-uniform in the molecule of aceperimidylene (LXVII), the positive π-charge on the $C_{(2)}$ atom of the latter being higher than in the molecule of compound (I). The maximum negative charge in aceperimidylene is concentrated in the CH=CH bridge[143].



(LXV) (LXVI) (LXVII)

The CNDO/2 method revealed an interesting feature in the polarisation of the electron cloud in perimidine and naphthoimidazoles. In conformity with the foregoing considerations concerning the characteristics of the π-electronic structure of the molecule of compound (I), it was found that the polarisation of the C=N bond in the latter is caused mainly by the shift of π electrons[141], while in naphthoimidazoles[142] and in benzimidazole[141] it is due to a shift of σ electrons.

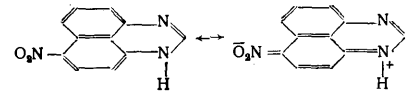
Quantum-mechanical calculations on 2-phenyl- and 2-2′-hydroxyphenyl-perimidines[138], the perimidinium cation[144], perimidone[145], and 2,3-dihydroperimidine[146] have also been published.

2. Colour and Electronic Spectra

One of the most interesting features of perimidine is its bright yellow colour, which sharply distinguishes it from the colourless naphthoimidazoles. The electronic spectrum of compound (I) consists of three absorption bands in the region of 400, 330, and 235 nm (the α-, β-, and γ-bands)[147]. The last two bands are highly intense ($\lg \varepsilon = 4.1$–4.6) and are also observed in the spectra of 2,3-dihydroperimidines and 1,8-naphthylenediamines[148]. The β-band is undoubtedly related to the transfer of the electron pair of the nitrogen atom to the antibonding π orbital of the naphthalene ring[148], while the γ-band is apparently due to the electronic transitions within the naphthalene ring itself. The absorption α-band, responsible for the colour of the perimidines, is of greatest interest. It has a reduced intensity ($\lg \varepsilon \cong 3.0$) and is usually manifested as a shoulder, which probably explains the lack of attention paid to it by a number of investigators[57,140]. The α-band persists in the spectra of perimidinium salts, i.e. it cannot be attributed to the $n \rightarrow \pi^*$ transition[147].

According to calculated data[138], the origin of the long-wavelength absorption band of perimidines is the π-electron transfer from the naphthalene ring to the heteroring[138]. Thus this band is due to charge transfer between the π-donor and π-acceptor components of the perimidine system, which is consistent with the high π-donor capacity of perimidines (see below) and explains qualitatively the influence of certain substituents on the colour of perimidines. Thus the decrease of the electron deficiency of the heteroring in compound (I) following the introduction of strong electron donors in the 2-position (amino- and alkoxy-groups, etc.) leads to the complete disappearance of colour[147]. Similarly the hydrogenation of the C=N bond leads to colourless compounds (2,3-dihydroperimidines). On the other hand, when strong π-acceptors are present in the 2-position in perimidine, the corresponding compounds are deeply coloured. Thus 2-benzoylperimidine is a dark wine-red[111], while 2-nitrophenyl and 2-nitrofuryl-perimidines are violet[32,93]. One may predict that a deepening of the colour should be observed also after the introduction of electron-donating substituents in the naphthalene ring; it is seen for aceperimidine as an example ($\lambda_{max} = 430$ nm) that this is indeed so.[147] The long-wavelength absorption band in the aceperimidylene spectrum is at 418 nm ($\lg \varepsilon = 4.1$).[143]

When groups containing vacant π orbitals are introduced into the *ortho*- and *para*-positions in the napthalene ring, the electronic spectra of perimidines change significantly and the colour deepens. An intense band due to the $\pi \rightarrow \pi^*$ transition appears in the long-wavelength region, its position depending on the electron-accepting properties of the substituent. For example, λ_{max} for 4-acetyl-1-methyl- and 9-acetyl-permidines are 405 and 416 nm respectively ($\lg \varepsilon =$ 4.11 and 4.0), while the values for 1-methyl-4-nitro- and 9-nitro-perimidines are 445 and 460 nm ($\lg \varepsilon = 3.96$ and 3.99).[148] When these groups are present in the 6- and 7-position, λ_{max} undergoes a further bathochromic shift. It is interesting to note that nitroperimidines are some of the deepest coloured nitro-compounds in the heteroaromatic series. The long-wavelength band in the spectra of these compounds is apparently of the type of the β-band and its strong bathochromic shift is caused by the ease of the transfer of electrons from the heteroring to the acceptor [structure (LXVIIIb)]:



(LXVIIIa) (LXVIIIb)

More detailed data on the ultraviolet spectra are given by Pozharskii et al.[149] for nitroperimidines, Minkin et al.[138] for 2-arylperimidines, Pozharskii and coworkers[147,150] for 2-aminoperimidines, and Pozharskii et al.[148] for 2,3-dihydroperimidines, perimidones, and thioperimidones.

3. π-Electron-Donating Properties

Perimidines tend to form deeply coloured charge-transfer complexes (CTC) with various π-acids, including weak acids such as 4-nitrobenzaldehyde[147]. The complexes usually have the 1 : 1 composition in the crystalline state. The charge-transfer bands for the CTC of perimidines and a number of related compounds with 1,3,5-trinitrobenzene (TNB) have been published[142,137,148] together with the ionisation potentials of the donors calculated from these data[147].

The high π-donor capacity of perimidines reflects the low ionisation potential of the electrons in the highest occupied π-MO. Calculations have shown that E^{π}_{HOMO} for the molecule of compound (I) lies appreciably higher than for naphthoimidazole molecules. In terms of the π-donor capacity, perimidines are superior not only to naphthoimidazoles and 1,8-naphthylenediamines but also to a well known π-donor such as phenothiazine. DHP, which apparently have a nearly planar structure in which the conjugation of the electron pairs of the heteroatoms with the aromatic ring is facilitated, exhibit the same π-donor capacity as perimidines[148].

It is of interest to note that, in contrast to the CTC of perimidines and 1,8-naphthylenediamines, the DHP complexes of two charge-transfer bands. In conformity with the experimental data and quantum-mechanical molecular orbital calculations, aceperimidylenes[143], perimidones, thioperimidones, and 2-imino-2,3-dihydroperimidines[148] are inferior as regards the π-donor capacity to perimidines and DHP. For a series of 2,3-dihydroperimidine structures[148], the ionisiation potentials in the gas phase have been measured

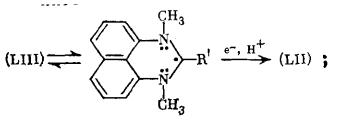
by the photoionisation method. The relative π-donor capacities of the perimidines can be estimated from the intensities of the peaks of the doubly charged ions in their mass-spectra[151].

4. Electron-Accepting Properties

In terms of their electron-accepting properties, perimidines occupy a position between azines and imidazoles. Thus perimidinium salts (LIII, R = CH_3) are reduced at the mercury dropping electrode with greater difficulty than the majority of the azinium cations but more readily than benzo- and naphtho-[1,2-*d*]imidazolium cations[152,153]. The ease of reduction of the naphtho[2,3-*d*]imidazolium cation is almost identical to that of the perimidinium cation. A correlation has been observed between the ease of the polarographic reduction of the above cations and the energies of their lowest vacant orbital[152].

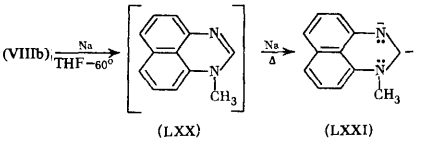
Perimidinium and naphtho[2,3-*d*]imidazolium salts are reduced with two single-electron diffusion processes, while benzo- and naphtho-[1,2-*d*]imidazolium salts are reduced with a single two-electron diffusion process. This indicates the relative stability of the radicals formed following the addition of the first electron to the perimidinium and naphtho[2,3-*d*]imidazolium cations. The structure of the radical in the case of perimidine is apparently close to that of (LXIX), i.e. the electron occupies an orbital localised in the heteroring. This is supported by the dependence of $E_{1/2}$ on the nature of the substituents in the heteroring of the perimidinium cation and by its low sensitivity to substituents in the naphthalene ring fragment.

The addition of the second electron leads ultimately to the formation of DHP:[152]



(LXIX) R = CH_3.

1-Alkylperimidine bases are not reduced polarographically, but, on treatment with sodium in tetrahydrofuran (THF) at −60 °C, compound (VIIIb) gives rise to the radical-anion (LXX), whose EPR spectra have been measured and whose spin density distribution has been calculated (it is a maximum in the 2- and 6-positions)[41]. When sodium is replaced by potassium under the same conditions or when sodium is used at a higher temperature, the dianion of 1-methylperimidine, whose structure is probably close to that of (LXXI), is formed:



(LXX) (LXXI)

5. Magnetic Properties and ^{1}H NMR Spectra

Compared with naphthoimidazoles, perimidines have a reduced diamagnetic susceptibility[147], which implies that the molecule of compound (I) is characterised by an appreciable polarisation paramagnetism as a consequence of the asymmetry of its π-electron cloud. The magnetic susceptibility data are consistent with the presence of a single EPR signal with a width of ~7 G for the crystalline specimens of the majority of perimidines; the signal intensity obeys the Curie law and corresponds to a single spin per 5000–10000 molecules[147]. The nature of the signal has been tentatively attributed to the presence at individual crystal lattice sites of local CTC, which is fully consistent with the electronic structure of perimidine.

The advances in the chemistry of perimidine are in many respects due to ^{1}H NMR. ^{1}H NMR data for perimidines are quoted in virtually all publications in recent years. They have been discussed in greatest detail by Pozharskii et al.[147] A characteristic feature of the ^{1}H NMR spectrum of compound (I) is the considerable upfield shift of the aromatic proton signals (on average by 0.8–1.2 p.p.m.) relative to naphthalene and naphthoimidazoles. This phenomenon is apparently due not so much to the weakness of the diamagnetic ring current as to the significant contribution of its paramagnetic component.

The $H_{(4)}$ and $H_{(9)}$ protons, whose signals are significantly displaced upfield compared with those of other protons, can be identified most readily in the ^{1}H NMR spectra of perimidines. As a consequence of the rapid exchange of the NH proton, in perimidines with a free NH group they become equivalent and are manifested by a quartet in a strong field. In 1-alkylperimidines these protons are no longer equivalent and give rise to two well resolved quartets, the quartet due to the $H_{(9)}$ proton being located in a higher field. The disappearance of one of these signals is significant evidence for the introduction of a substituent in the 4- or 9-position[146, 154]. The $H_{(5)}$–$H_{(8)}$ protons in the ^{1}H NMR spectrum of compound (I) give rise to a complex multiplet, which merges with the signal due to the $H_{(2)}$ proton. In the spectra of perimidinium cations the signal of the $H_{(2)}$ proton can be readily identified, since it is displaced downfield to a much greater extent than the signals of the other protons[114,115].

When even one electron-accepting group (acyl-,[144] nitro-,[155] or sulpho-group[156]) is introduced into the naphthalene ring in perimidines, the ^{1}H NMR spectrum is greatly simplified. In particular, this applies to the 6- and 7-positions, because the substituent usually deshields the second peri-proton, displacing its signal downfield and almost reducing to zero the constant J_{meta}. When these groups are in the 4- or 9-position, the structure of the compound is readily determined on the basis of the presence of a strong intramolecular hydrogen bond, the absence of a downfield shift of the signal due to the peri-proton, and by a number of other procedures[144,155]. However, in a few instances (*ortho*- and *para*-chloroperimidines[157]) the interpretation of the ^{1}H NMR spectrum is extremely difficult. The ^{1}H NMR spectra of aceperimidylenes[143] and 2,3-dihydroperimidines[101, 158] have been described. There are data on the ^{13}C NMR spectra of 2-azidoperimidines[159].

6. Infrared Spectra

The infrared spectra of compound (I), 2-methylperimidine, and certain 2-arylperimidines have been briefly discussed[138, 160]. There is information about the characteristic frequencies of other perimidines in almost every paper devoted to their synthesis. Infrared spectroscopy is the most important method for the identification of perimidines, particularly for their differentiation from the DHP, which are formed in many instances as side products or alternative reaction products. The 3100–3500 and 1500–1700 cm^{-1} regions of the spectrum, where the bands due to the stretching vibrations of the NH groups and the C=C and C–N bonds are located, are of greatest analytical importance for compounds of the perimidine series.

In the spectra of crystalline specimens of compound (I) and its 2-substituted derivatives there are no stretching vibration bands due to free NH groups. Instead there is a broad diffuse band extending from 3200 to 2500 cm^{-1}, which indicates the formation of stable associated species via intermolecular hydrogen sharp bonds. Bands due to the free ν(NH) vibrations in the form of a sharp intense peak at 3440 cm^{-1} appear in the infrared spectra of dilute solutions. The appearance of the ν(NH) band as a single sharp, frequently very intense, peak is observed sometimes also for crystalline specimens when the proton of the NH group is involved in an intramolecular hydrogen bond. The relevant data are available for 4(9)-nitro-,[155] 4(9)-acyl-,[144] and 2-(α-quinolinyl)-perimidines and also for 2,2'-diperimidine[101].

2,3-Dihydroperimidines with free NH groups do not undergo such strong association, which is undoubtedly due to their appreciably lower basicity. The ν(NH) stretching vibration bands in their spectra are manifested in both the crystalline state and in solution[101]. In the spectrum of the solution the ν(NH) band is appreciably less intense than for perimidines, is broader, and is displaced by 15–40 cm^{-1} towards lower frequencies.

In the range 1500–1700 cm^{-1} perimidines with a free NH group as a rule have three intense bands, among which the band with the highest wavelength is apparently due to the stretching vibrations of the amidine system. Indeed, in the spectra of perimidinium salts the ν(C$\overset{+}{\cdots}$N) band is displaced by 20–35 cm^{-1} towards higher frequencies, which is typical for cyclic amidines[155]. A very intense doublet is frequently present in the range 1580–1650 cm^{-1} in the spectra of 2-substituted perimidines instead of the triplet; DHP usually have a single intense band near 1600 cm^{-1} in the same region[138].

7. Ionisation Constants

In aqueous solutions $pK_a \cong 6$ for the perimidinium ion and its alkyl-substituted derivatives, i.e. perimidines are stronger bases than benzimidazole, naphthoimidazole and azines[161,162]. The basicity of DHP is lower by approximately two orders of magnitude in water[113] and by five order of magnitude in acetonitrile[163] than that of perimidines[164], which indicates the effective involvement of the electron pairs of both N atoms of DHP in conjugation with the π-electron system of the naphthalene ring and a considerable flattening of the heteroring. Data are available for the basicities of various 1-alkyl-[161,165] and 2-alkylperimidines[163,164,166], 2-arylperimidines[150], nitroperimidines[149], 2,3-dihydroperimidines[113,148], aceperimidines[161], and aceperimidylenes[143]. It is of interest that the basicity of the latter is lower by two orders of magnitude than that of perimidines.

8. Dipole Moments

The dipole moments of seven compounds of the perimidine series have been measured[138]: perimidine (3.18 D), 1-methylperimidine (3.48 and 3.66 D),[142] 2-methylperimidine (3.25 D), 2-phenylperimidine (3.03 D), 2-(4-nitrophenyl)perimidine (3.62 D), 2-(2'-hydroxyphenyl)perimidine (3.82 D), and 2-(2'-methoxyphenyl)perimidine (3.94 D). Quantum-mechanical calculations of the dipole moment of compound (I) have been carried out by the Hückel molecular orbital[138], Pariser–Parr–Pople[140], and CNDO/2 [141,142] methods, the last method yielding the best agreement with experiment. The fairly high dipole moment of compound (I) is consistent with the idea that its electronic structure is highly asymmetric.

9. Mass-Spectra

The mass-spectra of perimidines and 2,3-dihydroperimidine structures, including perimidone and thioperimidone, have been discussed in detail[151]. A distinctive feature of perimidines is their high stability with respect to electron impact and the presence in the mass-spectra of an extremely intense peak of a doubly charged molecular ion.

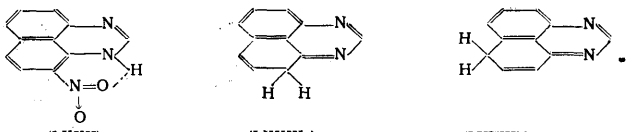
10. Fluorescence Spectra

The fluorescence of compound (I) and some of its derivatives has been studied[35,138]. It has been noted[35] that the overall fluorescence of perimidines is less intense than that of naphthoimidazoles. For the purpose of chromatographic separation, it is useful to know that simple perimidines virtually do not fluoresce on irradiation with u.v. light, while 2,3-dihydroperimidines and 1,8-naphthylenediamines do as a rule fluoresce. An extremely intense fluorescence is shown by 4(9)- and 6(7)-acylperimidines[145] and aceperimidylenes[143].

11. The Tautomerism of Perimidines

The set of all the physicochemical data shows that in perimidines, as in imidazoles, the NH proton rapidly migrates from one nitrogen atom to another (degenerate tautomerism of the amidine type). In monosubstituted permidines containing a substituent in the naphthalene ring there is no degeneracy and the two tautomers should have different properties. These differences are relatively small for 6(7)-substituted perimidines. Thus an estimate[149] based on the pK_a shows that the ratio of the 6- and 7-nitro-isomers in the equilibrium mixture is approximately 35 : 65.

On the other hand, the introduction of a nitro-group[149] or an acyl group[144,147] in the *ortho*-position displaces the equilibrium almost entirely in the direction of the 9-tautomer [for example, in the case of compound (LXXII)] as a result of the formation of a strong intramolecular hydrogen bond. The properties (solubility, basicity, and ultraviolet, infrared, and ^1H NMR spectra) of the 4- and 9-tautomeric forms correspondingly differ markedly. It is of interest that in 4(9)-chloroperimidines an intramolecular hydrogen bond is not formed between the chlorine atom and the NH group[157], apparently as a consequence of the instability of the five-membered chelate. On the other hand, the closure of the five-membered chelate ring in the direction of the 2-substituent has been shown to be possible by the infrared spectra of 2-(α-quinolinyl)perimidine and 2,2'-diperimidine[101]. Tautomerism with migration of the proton to the 4(9)- and 6(7)-positions is theoretically possible for perimidines. Although the 4*H*-perimidines (LXXIIIa) and 6*H*-perimidine (LXXIIIb) have never been detected, the derivatives of these tautomeric forms are known.



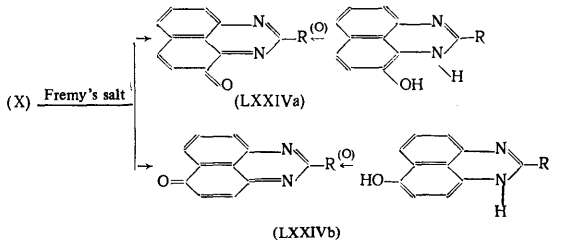
(LXXII) (LXXIIIa) (LXXIIIb)

IV. CHEMICAL PROPERTIES

1. Oxidation and Reduction Reactions

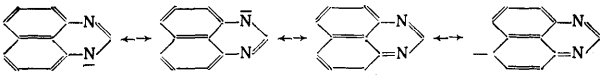
As a consequence of their high π-donor capacity, perimidines are extremely sensitive to the action of oxidants. Thus, under mild conditions Fremy's salt converts compound

(I) and its 2-substituted derivatives into a mixture of 4*H*-perimidin-4-one (LXXIVa) and 6*H*-perimidin-6-one (LXXIVb) in a high yield[91]. The ratio of the isomeric one-compounds is ~1 : 1 for 1- and 2-methylperimidines, but in the case of 2-phenylperimidine the 6-oxo-derivative predominates (3 : 1). This reaction has also been carried out for perimidines with alkyl substituents in the naphthalene ring and for certain 2,3-dihydroperimidines[91,168]:



The chemistry of compounds (LXXIV) is of interest particularly their interactions with nucleophiles, leading in many cases to perimidine derivatives which are otherwise extremely difficult to synthesise, e.g. 9-formylperimidines[169]. 4- and 6-Perimidones are also formed on oxidation of 4(9)- and 6(7)-hydroxyperimidines[21,121,122] by atmospheric oxygen or $FeCl_3$. The ease of autoxidation is a characteristic property of all perimidines containing $-E$-substituents in the 4(9)- and 6(7)-positions, where there is an excess of electrons. Apart from hydroxyperimidines, 4(9)- and 6(7)-aminoperimidines are very unstable in the form of bases[134]. If $-E$-substituents are in the 2-position with a deficiency of π electrons, the corresponding perimidines are entirely stable even in the form of bases. There is a qualitative relation between the ease of oxidation of various perimidines and the energy of the HOMO.[134]

The most important property of perimidine and many of its derivatives with a free NH group is the exceptional susceptibility of their N-anions to autoxidation[161]. According to data calculated by the Hückel molecular orbital method, the HOMO of the perimidine N-anion is antibonding ($E_{HOMO} = -0.284\beta$)[161]. This should increase the contribution of structures of type (LXXV, c and d) to the resonance hybrid of the *N*-anion. Presumably the oxidation of the *N*-anion begins with the formation of the corresponding radicals and results in the abstraction of a single electron from the HOMO and subsequent interaction of the radicals with oxygen or with another, as in the oxidative coupling of phenols:



(LXXVa) (LXXVb) (LXXVc) (LXXVd).

It is of interest that electron-accepting substituents in the 2-position (for example, Cl, CF_3, and C_6H_5) do not prevent the autoxidation of the corresponding anions, but, when $+E$-substituents are in the naphthalene ring (NO_2,[155] RCO,[144] SO_3H,[156] and CH=CH in aceperimidylene[143]), then the anion becomes stable in air. The monoanions of perimidone and thioperimidine are also stable, but their dianions undergo autoxidation[170]. In terms of the ease of oxidation of the *N*-anions, only phenothiazines approach perimidines[171]; the *N*-anions of other heterocycles with a pyrrole nitrogen atom are usually stable when acted upon by atmospheric oxygen.

1-Substituted perimidines are readily reduced by sodium in liquid ammonia by the Birch procedure[41], by lithium tetrahydroaluminate[113], or by tetrahydroborates in acid media[172] to 1-R2,3-dihydroperimidines (XXXVI). Perimidinium salts of type (LIII) are quantitatively reduced by alkali metal tetrahydroborates to the DHP (LII).[113]

2. *N*-Substitution Reactions at the Nitrogen Atom

Like imidazoles, perimidines are best alkylated in alkaline media and, in view of the possibility of the autoxidation of the *N*-anion, the process must be carried out in an inert atmosphere[161]. Primary alkyl bromides and iodides, including high-molecular-weight compounds, alkylate compound (I) in an alcoholic solution[36,161]. For alkyl halides with the iso-structure (for example, iso-C_3H_7X), the yield of 1-R-perimidine falls sharply[157,161]. Perimidine is also effectively methylated by dimethyl sulphate[172]. The use of methyl toluene-4-sulphonate[161,173] or diazomethane[161] yields less satisfactory results. For less reactive alkyl halides (for example, $ClCH_2CH_2CH_2NMe_2$), higher-boiling solvents (toluene, xylene, etc.) are sometimes used instead of alcohol[16,176].

N-Substitution reactions in the perimidine series are extremely sensitive to steric hindrance by 2- and 4(9)-substituents. Thus, although 2-methyl-, 2-ethyl-, and 2-phenyl-perimidines are methylated[43,46,173,177], they cannot be alkylated by benzyl chloride and isopropyl, allyl, and phenacyl bromides[174,175]. 4(9)-Substituted perimidines are alkylated only at the nitrogen atom remote from the substituent, while 1,4-disubstituted perimidines are not quaternised by methyl iodide even after prolonged heating[144,152,155,174]. The only exception proved to be 4-chloro-1-methylperimidine, which could be converted into a quaternary salt by prolonged refluxing with CH_3I in 18% yield[157].

The alkylation of 6(7)-monosubstituted perimidines gives rise to a mixture of 1,6- and 1,7-isomers which is difficult to separate and in which the 1,6-isomer predominates somewhat[178]. On quaternisation, both isomers yield the same quaternary salt[144,146,155]. The reduced yields of the alkylation products of 4(9)- and 6(7)-nitroperimidines are striking[155]. The explanation is apparently the reduced nucleophilicity of the corresponding anion. The anion of 2-methyl-6,7-dinitroperimidine is not methylated at all under these conditions, while the *N*-methyl derivative of this compound was obtained in a low yield via the silver salt[149]. Nor was it possible to methylate the anion of 2-trifluoromethylperimidine[24].

In its reactions with allyl and benzyl halides, the *N*-anion of perimidine exhibits its ambident properties [the contribution of structures of the type (LXXV, c and d) to the resonance hybrid] and the product of *C*-alkylation in the 4(9)-position is formed together with 1-allyl- and 1-benzylperimidines[174]. The best method for the benzylation of compound (I) apparently involves treating the latter with *N*-benzyl-*N*-methylmorpholinium chloride[165]. Another way of avoiding *C*-alkylation in the case of allyl and benzyl halides is to carry out the reaction without an alkaline agent in the presence of twice the amount of perimidine[174], the second equivalent of compound (I) being used to combine with a hydrogen halide molecule from the salt formed initially. This method is preferable when the alkylating agent or the reaction product is unstable in an alkaline medium ($RCOCH_2Br$, CH_3OCH_2Cl, etc.) or when the formation of an anion is difficult, for example, in the series of 9-acylperimidones, and also when the process must be carried out at an elevated temperature, for example, in the alkylation of 2-methyl- and 2-phenyl-perimidines.

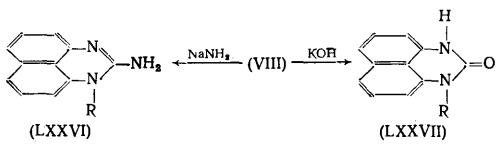
In contrast to imidazoles, perimidines do not undergo the Ullman arylation[161] and the only method of synthesising 1-arylperimidines involves the reaction of *N*-aryl-1,8-naphthylenediamines with carboxylic acids and their derivatives[16,17]. Perimidine and its 1- and 2-substituted derivatives undergo *N*-amination with formation of 2-aminoperimidinium salts[179]. Perimidines combine via the NH group with compounds containing multiple bonds; chlorotrifluoroethylene (1-β-chlorotrifluoroethylperimidine is formed)[180], acrylonitrile (1-β-cyanoethylperimidines are formed)[25,181], and formaldehyde

(1-hydroxymethylperimidine is formed)[161]. 2,2′-Diperimidine combines with a styrene molecule via the NH groups[40].

There are also data for the alkylation of aceperimidine[161] and its 2-methyl-,[46] 4-nitro-,[182] and 4-acetyl derivatives[134], [144], aceperimidylene[143], perimidones[183–186], and 1,3-disubstituted DHP.[172] Reactions involving the *N*-acylation of perimidone[183] and 1-R-2,3-dihydroperimidines have been described[114,172,187].

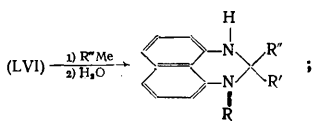
3. Reactions of Perimidines with Nucleophiles

Reactions with nucleophiles are extremely characteristic of *N*-substituted perimidines. They all involve the μ-carbon atom on which a high positive charge is concentrated. Thus 1-alkyl-,[88,188] 1-benzyl-,[88] 1-phenyl-,[16] 1-methoxymethyl-,[88] and 1-dialkylaminoalkyl-perimidines[16,176] undergo amination by sodium amide with formation of high yields of the amines (LXXVI) and hydroxylation by alkali with formation of high yields of the perimidones (LXXVII).[176,186,189] Both reactions are important in the perimidine chemistry. It must be emphasised that, in terms of the ease of hydroxylation, perimidines are superior to all other nitrogen heterocycles introduced into this reaction[186] and, in terms of the ease of amination, they are only slightly inferior to the most active heterocycles—isoquinoline and benzimidazole[190,191]. 1-R-Aceperimidines are also readily aminated[88] and hydroxylated[186]:



(LXXVI) (LXXVII)

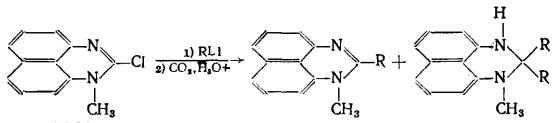
As regards their behaviour with respect to organometallic compounds, perimidines resemble more closely azines, to which organometallic compounds usually add, than heterocycles with an excess of π electrons and azoles (pyrrole, indole, and benzimidazole), which are metallated by these compounds. Thus 1-substituted perimidines[117], aceperimidines, and aceperimidylenes[119] react with organometallic compounds regardless of temperature and solvents, forming 2,3-dihydroperimidines (LXXVIII):



(LXXVIII) R = Alk or Ar; R′ = H, Alk or Ar; R″ = Alk, Ar, or heteroaryl.

Only in one case, in the reaction of compound (VIIIb) with n-butyl-lithium, was the formation of a small amount of the 2-lithio-derivative detected: carboxylation of the reaction mixture led to the isolation of 1-methylperimidine-2-carboxylic acid in 8% yield[117]. It is of interest that the two naphthoimidazoles isomeric with perimidine behave in different ways with organometallic compounds. While the derivative of the linear naphthoimidazole forms adducts with organometallic compounds, derivatives of the angular isomer are metallated by the latter[119]. The addition of organometallic compounds to perimidines is attributed to their reduced aromaticity, the high polarisation of the C=N bond, and the relatively low CH acidity (the rate of base-catalysed deuterium exchange involving the Cμ–H proton has been measured[119]).

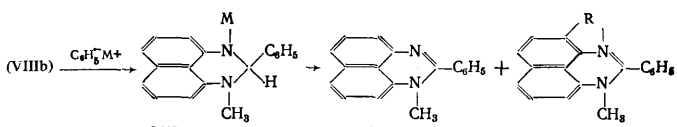
Alkali metal naphthalenides, which readily metallate azole rings, also fail to metallate compound (VIIIb).[141] Thus, treatment of compound (VIIIb) with lithionaphthalene in THF followed by treatment of the mixture with benzophenone or CO_2 gives rise to a mixture consisting of 1-methyl-2,3-dihydroperimidine and 1-methyl-2-(α-naphthyl)perimidine. The interactions of 2-chloro-1-methylperimidine (LXXIX) with butyl- and phenyl-lithium,[117] with alkali metals, and with alkali metal naphthalenides[41] were investigated as other possible synthetic pathways to 2-metalloperimidines. However, in these cases true metallation was not observed. Thus the reaction of compound (LXXIX) with butyl- or phenyl-lithium followed by treatment of the mixture with benzophenone or CO_2 yielded the following products:



(LXXIX)

The products of the interaction of compound (LXXIX) with lithionaphthalene proved to be compound (VIIIb), its 2,3-dihydro-derivative, and 1,1′-dimethyl-2,2′-diperimidine.

The use of benzophenone to bind 2-metalloperimidines which may be formed leads in many instances to extremely unexpected reactions. Thus, whereas compound (VIIIb) reacts with phenylsodium, forming 1-methyl-2-phenyl-2,3-dihydroperimidine in almost quantitative yields, treatment of the final mixture with benzophenone results in the formation of completely different products: 1-methyl-2-phenylperimidine (LXXX) and 1-methyl-2,4-diphenylperimidine (LXXXIa).[154] On the other hand, when phenylsodium is replaced by phenyl-lithium, the yield of compound (LXXX) falls and the main reaction product becomes the carbinol (LXXXb). Compound (XXX) is apparently formed as a result of the elimination of the metal hydride from the intermediate adduct (LXXXII) under the influence of benzophenone:



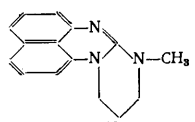
(LXXXII) (LXXX) (LXXXI)

(a) R = C_6H_5; (b) R = $(C_6H_5)_2COH$.

This is the only known reaction involving perimidines in which a nucleophile enters the naphthalene ring with its electron excess and not the 2-position.

2-Chloroperimidines, obtained by treating perimidones with phosphoryl chloride, are highly reactive in reactions with nucleophiles[88]. Their halogen is readily exchanged for the NH_2 group[88,192] and the primary[16,192] and secondary[176] amine residues can be exchanged for azido-,[147,159,193] alkoxy-, and hydrazino-groups[194]. The rates of the piperidinolysis reactions of 2-chloro-1-methyl derivatives of perimidine, naphtho[2,3-*d*]imidazole, and naphtho[1,2-*d*]imidazole are in the proportions 420 : 33 : 1, which corresponds to the positive charges on the $C_{(2)}$ atoms in these heterocyclic systems[195].

When an attempt was made to synthesise 2-chloro-2-(γ-dimethylaminopropyl)perimidine from the corresponding perimidone and $POCl_3$, the amine (LXXXIII) was obtained unexpectedly[16]:

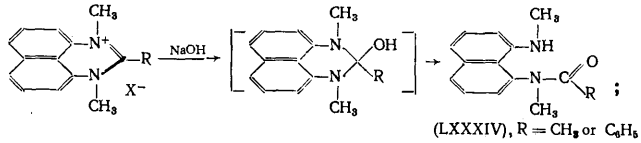


(LXXXIII)

4. The Interaction of Perimidinium Salts With Nucleophiles

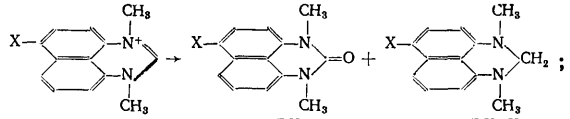
Compared with neutral perimidines, perimidinium salts exhibit a still greater reactivity in relation to nucleophiles. As already stated, they are readily reduced and readily

combine with organometallic compounds to form DHP.[117,196] The most important and interesting reactions of perimidinium salts are those under the influence of alkali agents. The salts substituted in the 2-position are converted into acyclic compounds (LXXXIV) on heating with alkalis, like imidazolium salts[46]:



(LXXXIV), R = CH_3 or C_6H_5.

However, 1,3-dialkylperimidinium salts without a substituent in the 2-position are almost quantitatively converted under these conditions into a mixture with the corresponding perimidone (LXXXVI) and 2,3-dihydroperimidine (LXXXVII), in which the perimidone may predominate somewhat; this reaction is of preparative value[146,156,158,178]:

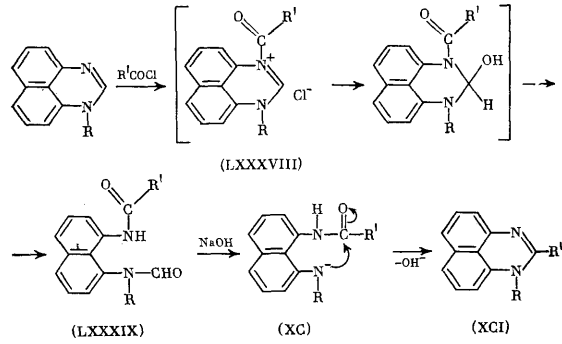


(LXXXV) (LXXXVI) (LXXXVII)

(a) X = H; (b) X = Cl; (c) X = NO_2; (d) X = CH_3CO; (e) X = SO_3^-.

Treatment of the 1,3-dimethylperimidinium cation with one mole of KNH_2 in liquid ammonia leads to results similar to those obtained on treatment with alkali, but the reaction with three moles of KNH_2 leads to the formation of 40% of *N,N'*-dimethyl-1,8-naphthylenediamine together with 1,3-dimethylperimidone[197].

The so-called recyclisation reaction is of very great synthetic importance in the perimidine chemistry[198,199]. Its principle is that treatment of 1-R-perimidines with aromatic, heteroaromatic, or vinylaromatic acids in the presence of mild bases (for example, triethylamine) results in the formation, via a stage involving the formation of *N*-acylperidinium salts (LXXXVIII), of *N*-acyl-*N'*-formyl-1,8-naphthylenediamines (LXXXIX), which recyclise on subsequent heating with alkali with elimination of the formyl group from the pseudo-base (XC) and the formation of a 1,2-disubstituted perimidine (XCI) containing in the 2-position the residue of the acid whose chloride had been used initially:



(LXXXVIII)

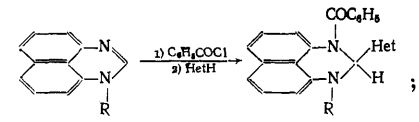
(LXXXIX) (XC) (XCI)

The reaction proceeds as a rule without side processes and has a high overall yield.

When compounds (LXXXIX) are heated with acids, the aroyl group is split off and the initial perimidine is reformed. On the other hand, when the deformylated pseudo-base (XC) is treated with an acid, it cyclises to compound (XCI), which is important for the synthesis of 1,2-diarylperimidines[165].

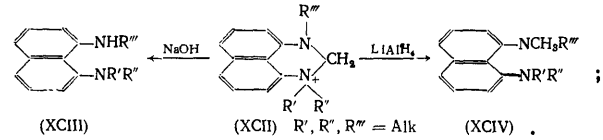
Derivatives of 2-phenylperimidine (XCI, R = C_6H_5) containing the following substituents R in the 1-position have been obtained in this way: methyl[198–200], allyl[174], benzyl, acetonyl, phenacyl, phenyl, methoxymethyl[165], and cyanoethyl[181]. The recyclisation of 1-methyl-, 1-(β-dialkylaminoethyl)-, and 1-(γ-dimethylaminopropyl)-perimidines by the chlorides of other carboxylic acids made it possible to introduce in the 2-position the halogenophenyl[38,199,200], methoxyphenyl[198–200], nitrophenyl[200], 3,4-methylenedioxyphenyl[200], α-naphthyl[41], α-furyl, α-thienyl[198,199], styryl, and β-(5-furyl)vinyl groups[198], as well as many other substituents. The recyclisation reaction also takes place with aceperimidines [198,199] and 1,9-trimethyleneperimidine[201]. However, it could not be achieved for benzo- and naphtho-imidazoles as well as perimidines with electron-accepting groups in the naphthalene ring (Cl, NO_2, and RCO).

The salts (LXXXVIII) obtained *in situ* undergo substitution by heteroaryl groups by reaction with heterocycles with an excess of π electrons[187]:



Het = 2-pyrrolyl or 3-indolyl.

1,1,3-Trisubstituted 2,3-dihydroperimidinium salts (XCII) are readily converted into tri-*N*-substituted salts (XCIII) on treatment with an excess of alkali, while their reduction with $LiAlH_4$ leads to tetra-*N*-substituted 1,8-naphthylenediamines (XCIV), which constitutes the best method of synthesising these compounds. For R''' = CH_3CO in the salts (XCII), treatment with alkali is accompanied by the elimination of the acetyl group and the formation of 8-dialkylamino-1-aminonaphthalenes (XCIII, R''' = H):[172]



(XCIII) (XCII) R', R'', R''' = Alk (XCIV).

On heating with elemental sulphur, perimidine and its derivatives are converted into thioperimidones[88,185].

5. Electrophilic Substitution Reactions

Perimidine is one of the most active heterocycles in relation to electrophiles, which can be explained by its high π-donor capacity and high negative π-electronic charge in the *ortho*- and *para*-positions of the naphthalene ring. Electrophilic substitution reactions involve precisely these positions; hitherto attacks by electrophiles on the 5- and 8-positions are unknown.

Electrophilic substitution reactions of perimidines are very sensitive to steric hindrance by the *N*-substituent. Very small species (D^+ and with much difficulty Cl^+) can enter the 4- and 9-positions in the presence of neighbouring *N*-methyl groups.

(a) Acid Deuterium Exchange

Perimidine, its 1- and 2-methyl derivatives, and 2-imino-1,3-dimethyl-2,3-dihydroperimidine do not undergo deuterium exchange on prolonged refluxing in CF_3COOD or CD_3COOD, as they exist exclusively in the cationic form under these

conditions. For deuterium exchange to become possible, the basicity of the compound must be lower than that of compound (I) by at least 2–3 pK_a units. This condition is satisfied particularly by 2-trifluoromethylperimidine (pK_a = 6.64 in acetonitrile) and 2-difluoromethylperimidine (pK_a = 8.90), which slowly exchange protons for deuterium on heating in CD_3COOD, but not by 2-fluoromethylperimidine (pK_a = 11.87), where only the protons of the CH_3 groups are exchanged under these conditions[166].

Deuterium exchange involving compound (I) and its alkyl derivatives takes place in concentrated D_2SO_4, but the reaction is complicated by the simultaneous sulphonation[156]. The H–D exchange involving compound (I) in the naphthalene ring can proceed via the *N*-anion (in C_2H_5OD), using its ambident properties. The reaction is slow and involves only the *ortho*-positions[166].

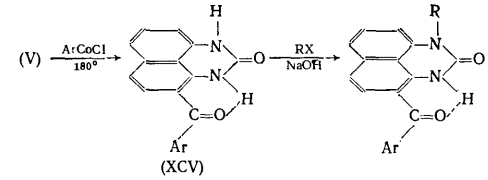
(b) Acylation

Perimidine is apparently the only heteroaromatic system with a pyridine nitrogen atom which undergoes Friedel–Crafts acylation comparatively readily. It is best to carry out the acylation with the aid of carboxylic acids in polyphosphoric acid (PPA). For compounds with an unsubstituted NH group, the reaction is clearly subject to kinetic and thermodynamic control. Mainly the 6(7)-acyl derivative (55–85%) is formed at 70–85 °C together with a small amount of the 9-isomer. At 120–150 °C the only reaction products become 4(9)-acylperimidines[144]. One of the causes of the increased stability of the latter is the presence of a strong intramolecular hydrogen bond.

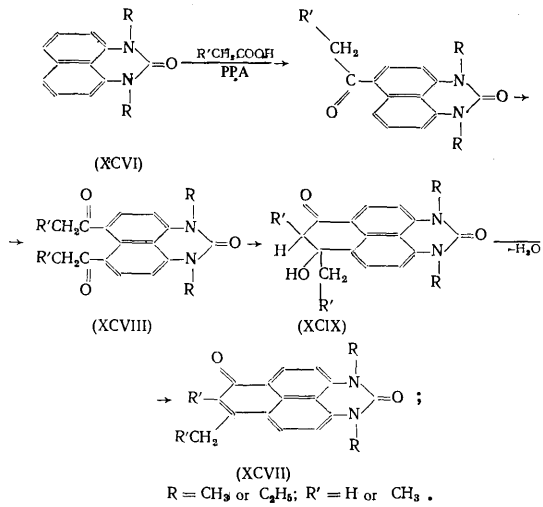
1-Methylperimidine is acetylated with formation of a mixture of 6-, 7-, and 4-acetyl derivatives, which is difficult to separate and in which the first two isomers predominate appreciably. 2-Perfluoroalkylperimidines have certain unusual features[163]. They are not acetylated by carboxylic acids in PPA but undergo trifluoroacetylation extremely readily, without a catalyst, by trifluoroacetic anhydride (their acylation by the chlorides of perfluorocarboxylic acids is also possible, but the reaction is slow). Compounds with a free NH group then form only 9-acyl derivatives, while trifluoroacetylation of 1-methyl- and 1-phenyl-2-trifluoromethylperimidines proceeds with a high yield only in the 7-position[163]. On passing from 2-trifluoromethylperimidine to the more basic 2-difluoromethyl- and 2-fluoromethyl-perimidines, the trifluoroacetylation of the naphthalene ring proceeds with increasing difficulty, while compound (I) and its alkyl derivatives are not acylated at all by trifluoroacetic anhydride[163,166]. It is noteworthy that the 1,3-dimethylperimidinium cation is acetylated in the 6(7)-position with the CH_3COOH–PPA mixture under the same conditions as perimidine[178].

1,3-Dimethylperimidone is acylated quantitatively by trifluoroacetic anhydride in the 6-position[163]. The same product is obtained from the thione (LIV) under the same conditions. In the latter case the reaction is apparently also directed to the sulphur atom, after which the thiuronium salts formed hydrolyses to the corresponding perimidone (cf. Borovlev and Pozharskii[145]). On treatment with $(CF_3CO)_2O$, 1,3-dimethyl-2,3-dihydroperimidine chars, but careful acetylation of 1,2,2,3-tetramethyl-2,3-dihydroperimidine made it possible to obtain its 6-trifluoroacetyl derivatives in 21% yield[163].

It has been reported that unsubstituted perimidone (V) is acylated by benzoyl chloride in the presence of $AlCl_3$, but the structure of the product was not established[202]. It was shown later that satisfactory results are obtained in the acylation of compound (V) by aroyl chloride without a catalyst at 180 °C. The reaction product, which is the 4(9)-aroyl derivative (XCV), was subsequently alkylated in order to obtain dyes[183]:



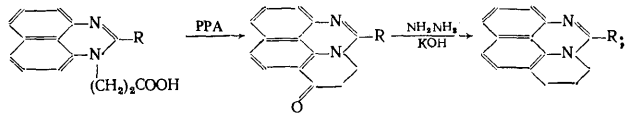
The acylation of compound (V) by carboxylic acids in PPA leads to a mixture of its 4(9)- and 6(7)-acyl derivatives[185]. The acylation of 1,3-dialkylperimidones takes place only in the *para*-positions. When acetic and propionic acids are used, the reaction products are the monoacyl derivatives (XCVI) and phenalenones (XCVII).[145,185] It has been established[145] that phenalenones are formed via stages involving the diacylation and crotonylation of the diacyl derivatives (XCVIII) which, like th aldol (XCIX), could be isolated in special experiments. In those cases where aldol condensation is impossible (for example, in benzoylation), the isolation of a diacyl derivative does not present a problem[145]:



R = CH_3 or C_2H_5; R' = H or CH_3.

Under analogous conditions, 1,3-dimethyl-2,3-dihydroperimidine and the thione (LIV) do not form pericyclisation products and the reaction proceeds only up to the 6(7)-acyl derivative, which is consistent with the lower reactivity of dihydroperimidines and thioperimidones in acylation reactions compared with perimidones[145,185]. Other methods have also been developed for building the phenalenone ring onto perimidones, thioperimidones, and 2,3-dihydroperimidines[145].

In the series of perimidines and perimidones there is a possibility of intramolecular acylation reactions[181,201]; the resulting ketones can be converted by the Wolff–Kishner reaction into bridged systems, for example:



R = H, CH_3 or C_6H_5.

The unsubstituted perimidone undergoes simultaneous acylation by malonic acid diesters in the 1- and 9-positions[203].

The problems concerning the acylation of aceperimidines have been considered[144].

(c) Nitration

Depending on the amount and concentration of nitric acid, perimidines are nitrated (most effectively in acetic acid) to mono-, di-, and tri-, and tetranitro-derivatives[155], while aceperimidines are nitrated to the mono- and di-nitro-derivatives[182]. The initial nitration of perimidines with a free NH group is accompanied by charring, which reduces the yield, particularly for perimidine itself. Thus perimidine is nitrated on treatment with 1 mole of HNO_3 to 4(9)- and 6(7)-nitro-derivatives in proportions of 2.5 : 1 with an overall yield of 30%. Under the same conditions, aceperimidine gives rise to 50% of the 4(9)-nitro-derivative and 17% of the 4,9-dinitro-derivative, while 2-methylperimidine gives rise to the 4(9)- and 6(7)-nitro-derivatives in proportion of 1 : 2.5 with an overall yield of 64%. The nitration of mono-, di-, and tri-nitroperimidines proceeds without charring. When 1- and 2-methylperimidines are nitrated with 2 moles of HNO_3, a mixture of three dinitro-compounds, namely the 6,9-, 6,7-, and 7,9-dinitro-derivatives, is formed in yields of 40, 20, and 10% respectively. Nitration of compound (II) yields 4,9-dinitroaceperimidine. When an eightfold excess of HNO_3 is used, a mixture of 4,6,9- and 6,7,9-trinitroperimidines is formed, in which the second isomer predominates. By heating this mixture with an excess of fuming HNO_3, it is possible to obtain 4,6,7,9-tetranitroperimidines in yields up to 90%.[155,182]

It appears that only the initial nitration of perimidine proceeds via the cation. Indeed the 1,3-dimethylperimidinium cation is nitrated in the 6-position to the mononitro-derivative under the same conditions as perimidine[178]. However, the 6-nitro-1,3-dimethylperimidinium cation gives rise to only traces of the dinitro-compound on prolonged refluxing with fuming HNO_3.[149]

1-Methylperimidine is nitrated mainly in the *para*-positions, the yield of the 4-nitro-derivative amounting to only 9%.[155] The nitration of 1-methyl- and 1,2-dimethyl-aceperimidines[182] and 2-aminoperimidine[204] has also been described.

One of the most interesting features of perimidines and aceperimidines is the possibility of nitrating them with alkali metal nitrates in acetic acid[205]. The reaction takes place readily even at room temperature and makes it possible to introduce up to three nitro-groups into the naphthalene ring. For example, 2-methyl-6,7-dinitroperimidine is converted by 1 mole of $NaNO_2$ into 2-methyl-6,7,9-trinitroperimidine in 79% yield. In mono- and di-nitration the yields are higher owing to charring. The mechanism of the nitration of perimidines by nitrites is not altogether clear. It is striking that this reaction has been encountered also for a number of other polynuclear heterocyclic systems with a π-electron-donating capacity (phenothiazines[206] and porphyrins[207]), which suggests that the proccess may have a possible radical-cation mechanism[206,207]. Perimidines are extemely readily nitrated with nitrogen dioxide as far as the tetranitro-derivatives[205].

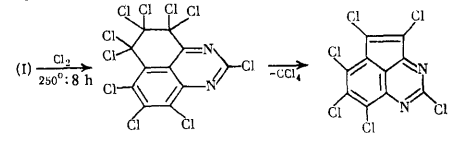
(d) Halogenation

The chlorination of perimidines[157], perimidones, and dihydroperimidines[146] with sulphuryl chloride in acetic acid and with *N*-chlorobenzotriazole (CBT) in an aprotic medium has been investigated. The chlorination of perimidine itself with 1 mole of SO_2Cl_2 leads to the formation of the 6(7)- and 4(9)-chloro-derivatives in proportions of 8 : 1. Treatment with 2 moles of SO_2Cl_2 results in the formation of a complex mixture of mono-, di- and tri-chloroperimidines, while treatment with 3 moles of SO_2Cl_2 gives rise to 4,6,7-trichloroperimidine in a high yield. Tetrachloroperimidine could not be obtained with the aid of SO_2Cl_2, while 2-methylperimidine is chlorinated to the tetrachloro-derivatives with an excess of SO_2Cl_2.

Fundamentally different results have been obtained with CBT. On treatment with CBT, perimidines with a free NH group undergo extensive oxidation, but 1-R-perimidines are chlorinated very smoothly by this reagent. The reaction initially involves the *ortho*-positions and only then are the *para*-positions substituted. Thus the reaction of compound (VIIIb) with 1 mole of CBT in chloroform at 0 °C gives rise to a mixture of 9-chloro-, 4-chloro-, and 4,9-dichloro-derivatives, while the reaction with 2 moles of CBT leads to only the 4,9-dichloro-derivative[157]. Subsequent chlorination yields the 4,7,9-trichloro- and then the 4,6,7,9-tetrachloro-derivatives. Analogous results have been obtained in the chlorination of 1,2-dimethylperimidine and 6,7-dichloro-1-methylperimidine with CBT. The steric hindrance to substitution in the 9-position in 1-isopropylperimidine is too great and the exhaustive chlorination product is 4,6,7-trichloro-1-isopropylperimidine[157].

The sharp difference in the mode of the initial attack between the reactions with SO_2Cl_2 and CBT can apparently be explained by the fact that the reaction proceeds via the cation and the base in the former and latter cases respectively. Indeed the 1,3-dimethylperimidinium cation is chlorinated mainly in the *para*-positions by both reagents[146]. 1,3-Dimethylperimidone is chlorinated with CBT initially also in the 4- and 9-positions and it was impossible to stop the reaction at the monochlorination stage. On treatment with CBT, 1,3-dimethyl-2,3-dihydroperimidine chars, while with the aid of SO_2Cl_2 initially the *ortho*-positions and then the *para*-positions can be chlorinated[146].

The chlorination of perimidine with liquid chlorine in an autoclave at 250 °C has been reported[208]. The reaction product was perchloro-5,6-dihydro-4*H*-perimidine (C), which was subsequently converted into a quinazoline derivative (CI):

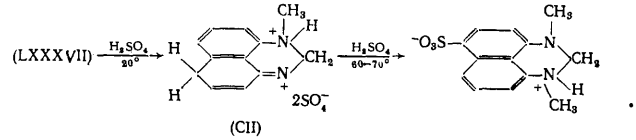


(C) (CI)

Very little is known about the bromination of perimidines. When 2-methylperimidine was treated with bromine in acetic acid, only the mono- and di-bromo-derivatives were obtained, but their structure was not established[44]. The nitration of the hydrobromide of 2-aminoperimidine involves the introduction of bromine into the naphthalene ring together with nitro-groups[204].

(e) Sulphonation

Perimidine and its 2-substituted derivatives are sulphonated with concentrated H_2SO_4 even at 20 °C and below. The reaction is rapid and perimidine-6-sulphonic acids, which exist in a betaine form, are formed in a quantitative yield after 10–15 min[36,156]. With increase of reaction time, further sulphonation takes place, but the polysulphonic acids could not be isolated in a pure form[156]. The sulphonation of the 1,3-dimethylperimidinium cation and 1,3-dimethylperimidone also takes place readily, but 1,3-dimethyl-2,3-dihydroperimidine is sulphonated only at a temperature not less than 70–80 °C as a consequence of the formation of the dication (CII):[156]



(CII)

(f) Azo-coupling

As shown in an early study by Sachs[6], perimidines are excellent azo-components and give rise to blue azo-derivatives on treatment with diazonium salts. The reaction proceeds in the *para*-positions and has been described for perimidine itself and its 2-substituted derivatives[209], 6(7)-chloroperimidine[20], and 2-aminoperimidine[210].

(g) The Reactivity Indices and the Mode of Electrophilic Attack

According to quantum-chemical molecular orbital calculations, the *ortho*-positions in the perimidine molecule and in the perimidinium cation have a higher negative π-electronic charge than the *para*-positions (see above). Nevertheless, as can be seen from the foregoing, the vast majority of electrophilic reactions of perimidines take place initially in the 6- and 7-positions. It has therefore been suggested[144] that the electrophilic substitution reactions of perimidines are controlled by the cation localisation energies rather than the π-electronic charges. Indeed, the latter are appreciably smaller than in the *para*-positions both in the perimidine base and in its cation[144]. However, the localisation energies do not explain why the chlorination of perimidines with CBT, which probably proceeds via the uncharged form, is initially directed to the *ortho*-positions. This suggests that the charges nevertheless play a decisive role (in the absence of steric effects) in electrophilic substitution in perimidine bases, while the *ortho*-substitution in the cation is significantly counteracted by the field effect, which is not taken into account in molecular orbital calculations on isolated molecules. The study of other electrophilic substitution reactions involving unsubstituted perimidine is extremely desirable in this connection.

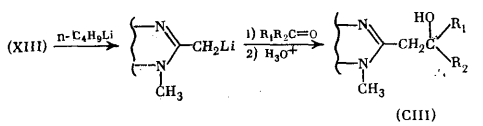
6. The Properties of Certain Functional Groups in Perimidine Derivatives

The perimidine nucleus exerts an appreciable influence on the properties of the functional groups linked to it.

(a) 2-Methylperimidines

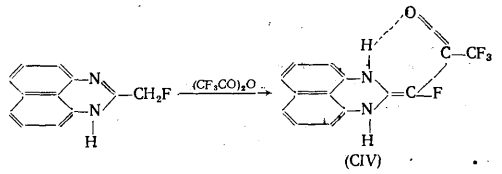
The hydrogen atoms of the CH_3 group in these compounds are characterised by a considerable mobility. Thus, according to the results of a study of the base-catalysed H–D exchange involving the 2-methyl group in 1,2-dimethylperimidine, the kinetic acidity of the methyl group is higher than in 1,2-dimethyl derivatives of imidazole, naphtho[1,2-*d*]imidazole, benzimidazole, and naphtho[2,3-*d*]imidazole by 3.9, 3.2, 2.3, and 0.3 orders of magnitude respectively[196], which agrees with the decrease of the positive charge on the $C_{(2)}$ atom in the above series.

When compound (XIII) is treated with n-butyl-lithium, the CH_3 group is metallated, which has been used for the synthesis of the carbinols (*CIII*):[196]



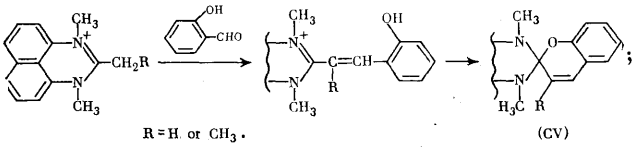
(CIII)

2-Fluoromethylperimidine, where, in contrast to 2-methyl- and 2-difluoromethyl-perimidines, the protons of the CH_2 group exchange for deuterium on heating in CD_3COOD and undergo trifluoroacetylation on treatment with $(CF_3CO)_2O$,[166] exhibits an unexpectedly high reactivity in relation to electrophiles. The product of the last reaction exists in the tautomeric methide form (CIV) stabilised by an intramolecular hydrogen bond. Similar chelates are characteristic also of other perimidines in which one or two protons of the 2-methyl group have been substituted by acidifying substituents:



(CIV)

2-Methylperimidines condense in the absence of a catalyst with various aldehydes, forming 3-styrylperimidines[211–213]. If the aldehyde contains an electron-accepting substituent (e.g. NO_2), the reaction can be stopped at the stage involving the formation of the corresponding carbinols[211]. 2-Methylperimidinium salts have also been introduced into this reaction[173,214]. In particular, the spiropyrans (CV) have been obtained by this method from salicylaldehyde and 2-hydroxy-1-naphthaldehyde[43]:

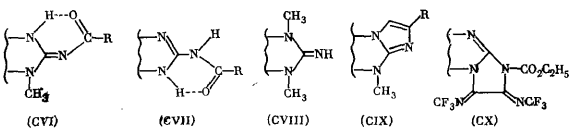


R = H or CH_3. (CV)

5-Nitrosalicylaldehyde forms in this reaction merocyanine, which could not be converted into a spiropyran.

(b) 2-Aminoperimidines

In connection with the amine–imine tautomerism of 2-aminoperimidines, their basicities and electronic and infrared spectra have been investigated[150,192]. At the same time studies have been made of the analogous properties of the fixed amine and imine models. Compared with the majority of other heteroaromatic amines, including 2-aminoimidazoles, 2-aminoperimidines exhibit a much greater tendency towards a shift of the equilibrium in the direction of the imino-form, whose concentration reaches 2%.[150] 1-R-2-Acylaminoperimidines and aceperimidines exist entirely in the imino-form (CVI), but, in the absence of a substituent in the 1-position, the amino-form (CVII) persists[215]. In both cases the preferred tautomer is stabilised by an intramolecular hydrogen bond.



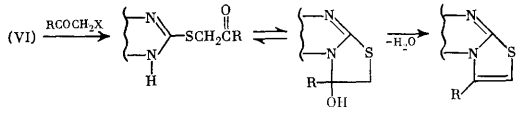
(CVI) (CVII) (CVIII) (CIX) (CX)

In their chemical behaviour 2-aminoperimidines in general resemble other heteroaromatic amines. Their alkylation in a neutral medium involves the pyridine nitrogen atom and makes it possible to obtain imines of type (CVIII).[216] There is also a possibility of the alkylation of the amino-group to 2-alkylamino- or 2-dialkylamino-perimidines, which is achieved by carrying out the reaction in liquid ammonia in the presence of potassium amide[217–219]. 2-Aminoperimidines are acylated at the amino-group with formation of compound (CVI) or (CVII),[192,215] but they form azomethines with a great deal of difficulty[216], while their interaction with α-halogenocarbonyl

compounds readily converts them into derivatives of imidazo-[1,2-*a*]perimidine (CIX).[220] The synthesis of compounds (CX) from perimidine-2-methylcarbamate has been described[221].

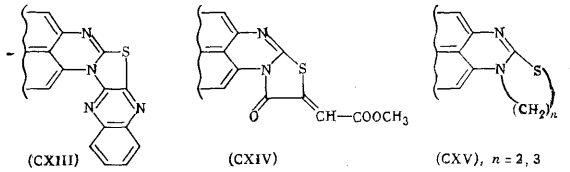
(c) 2-Mercaptoperimidines

Thioperimidone (VI) is acylated by α-halogenocarbonyl compounds at the sulphur atom with formation of compound (CXI).[222–225] The latter exists predominantly in the acyclic form (CXIa) but the cyclic structure (CXIb) predominates for R = H, CH_3, or C_2H_5.[222] When compound (CXIb) is treated with dehydrating agents, derivatives of thiazolo[3,2-*a*]perimidine (CXII) are formed[223–225]:



(CXIa) (CXIb) (CXII)

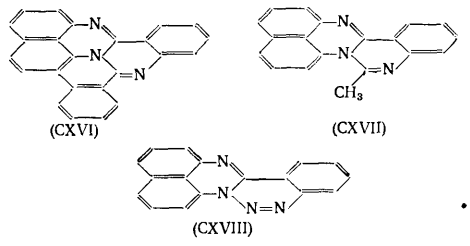
The reaction of compound (VI) with 2,3-dichloroquinoxaline[226], dimethyl acetylenedicarboxylate[227] or α,ω-dihalogenoalkanes[228] leads to the formation of compounds (CXIII)–(CXV) respectively.



(CXIII) (CXIV) (CXV), $n = 2, 3$

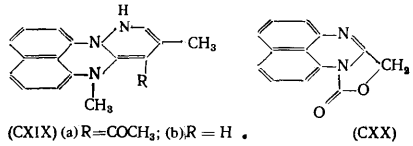
(d) Other Compounds

A series of bridged heterocyclic systems (CXVI)–(CXVIII) have been obtained from 2-(2′-aminophenyl)perimidine: compound (CXVI) has been synthesised by heating 2-(2′-benzamidophenyl)perimidine with $AlCl_3$,[229] compound (CXVII) has been obtained by heating 2-(2′-acetamidophenyl)perimidine with acetic anhydride, and compound (CXVIII) has been obtained by diazotising 2-(2′-aminophenyl)perimidine[32]:



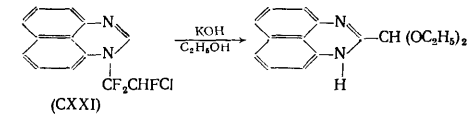
(CXVI) (CXVII) (CXVIII)

On treatment with acetic anhydride in the presence of potassium carbonate, the 1,3-dimethyl-3-aminoperimidinium salt gives rise to a derivative of pyrazolo[2,3-*a*]perimidine (CXIXa), which is deacylated on heating with HCl to form compound (CXIXb).[175] On treatment with chlorocarbonic ester in the presence of NaH, 2-hydroxymethylperimidine is converted into compound (CXIX):[26]



(CXIX) (a) R=$COCH_3$; (b) R = H (CXX)

An interesting recyclisation reaction has been observed on heating compound (CXXI) in an alcoholic solution of KOH:[180]



(CXXI)

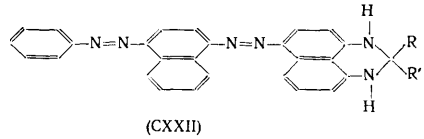
The reduction of the ethyl ester of perimidine-1-acetic acid to 1-(β-hydroxyethyl)perimidine and of 2-(2-furyl)perimidine to 2-(2-tetrahydrofuryl)perimidine has been described[25]. The 6(7)-trifluoroacetyl derivatives of perimidones and *N*-substituted perimidines are converted on heating with aqueous alkali into perimidone-6-(7)-carboxylic and perimidine-6(7)-carboxylic acids[166].

Studies of 2-azidoperimidines have shown that they exist in the form of tetrazolo[1,5-*a*]perimidines[159,193].

V. PRACTICAL APPLICATIONS

Numerous patents for the use of alkyl, aryl, azo-, sulpho-, and acyl-derivatives of perimidine, their quaternary salts, and perinones as dyes were issued in the first quarter of the present century. Although the structure attributed to the dyes was incorrect and in many instances still remains unelucidated (for example, the structure of the product of the interaction of 2-methylperimidine with phthalic anhydride)[7], many of them have found practical applications. The bibliography of the publications on this subject up to 1956 can be found in Richmond's review[5]. During the last 25 years, the salts of 2-styrylperimidines[213,230,231] and dispersed dyes based on 4(9)-aroylperimidones[184], *N*-aroylperimidones[232], phthaloylperimidones[233], 6(7)-azoperimidines[209,234], the amides of perimidine-6,7-dicarboxylic acid[127–129,235] and perimidone-6,7-dicarboxylic acid[236], and perinones[130,237] have been proposed as dyes for synthetic fibres.

Azodyes of the type of Sudan Black B with structure (CXXII) have found extensive applications in recent years in the dyeing of various fibres[238–242], as additives to liquid crystal displays[243], and in many other instances[244–249]:



(CXXII)

Phenalenones of type (CXVII) have been proposed as phosphors with a high fluorescence quantum yield[250–252], while perimidine and its 1- and 2-alkyl(aryl)-derivatives have been suggested as cationo-active additives to solutions for contact copper-plating of aluminium[253]. Perimidine-6(7)-sulphonic acids containing in the 2-position hydrophobic groups, a high-molecular-weight alkyl group, or a perfluoroalkyl group exhibit an appreciable antistatic activity[36]. By virtue of the exceptionally low solubility in water of its sulphate and the stability of its colloidal solutions, 2-aminoperimidine has recently found applications as a highly sensitive reagent for the determination of sulphuric acid[254] and sulphates[255] in air (for a complete bibliography, see Ishikawa et al.[79]).

2-Amino-6(7)-[4-acetophenylazo]perimidine[210] has been suggested as a reagent for the determination of microamounts of SO_3^{2-} ions and perimidine itself has been suggested as a reagent for the gravimetric determination of copper[256]. 1,3-Di(β-hydroxyethyl)perimidone is used in the manufacture of polyester fibres[257].

Numerous communications have been devoted in recent years to the biological activity of perimidines. Various 1- and 2-substituted perimidines have been proposed as highly effective antiulcer agents[26,258-265] and neurotropic preparations (both depressants and stimulants of the central nervous system have been discovered[16,109,134,175,177,200]). 2-Arylperimidines exhibit carcinostatic activity[266]. A moderate or weak antimicrobial activity of 2-aminoperimidines[216], the anoretic activity of compounds (CXII) and (CXV),[228] and the antihelminthic activity of 2-acyl-amino-[84] and 2-styryl-perimidines[212] have been reported. Certain perimidines exhibit an extremely marked fungicidal activity[83,191].

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The Basicity and Nucleophilicity of Arsenyl Compounds†

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Data are presented on the nature of the As=O bond in compounds of tetracoordinate arsenic. Problems associated with the manifestation of the electron-donating properties of arsenyl compounds, particularly their basicity in various media as well as their proton-accepting capacity in the formation of hydrogen-bonded complexes, are examined. The electron-donating and proton-accepting capacities of compounds of the type R_nEO, where E=N, P, As, Sb, S, Se, or Te, are compared. The reactions of arsenyl compounds with a wide variety of electrophiles as well as other reactions involving the arsenyl group are discussed. The bibliography includes 172 references.

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I. INTRODUCTION

A large amount of scattered data have now accumulated on the physicochemical and chemical properties of tetracoordinate arsenic compounds containing the arsenyl group. There are no reviews wholly devoted to this problem, but compounds containing the arsenyl group have been mentioned in monographs[1-4], reviews[5-18], and dissertations[19,20].

Substances containing the As=O bond constitute one of the most numerous groups of organoarsenic compounds, which play an important role both in laboratory practice and in certain branches of the economy (for example, as extractants in hydrometallurgy, medicinal preparations, herbicides, etc., [21,22]). Furthermore, the characterisation of the structure and properties of arsenyl compounds makes a definite contribution to the understanding of the structure and reactivity of compounds containing the E=O bonds (E=C, Si, P, Se, Te, etc.).

The aim of the present review is to survey the literature data, mainly for the last ten years, concerning the nature of the As=O bond as well as the basicity and nucleophilic reactivity of compounds of tetracoordinate arsenic. The nucleophilic properties of these compounds as well as their basicity, which, according to Edwards and Pearson[23], is a special case of the manifestation of nucleophilic reactivity, are determined by the presence of the arsenyl group. The review does not deal with methods for the synthesis arsenyl compounds, because these have been published in monographs[1-4] or, with their complex formation reactions with various metal salts, since the literature on this problem is extensive and its survey should be the subject of a special review.

Table 1. Certain physical characteristics of the As=O bond.

Type of compound	Compound	r (As=O) (r (As–O)), Å	$\nu_{As=O}$, cm^{-1}	$k_{As=O}$, mdyn Å^{-1}	Bond order	μ, D	$\mu_{As=O}$, D
Tertiary arsine oxides	Me_3AsO	1.65 [31]	903 [35]	7.24 [24]	1.50 [30]	—	—
ditto	Me_3AsO	1.62 [30]	—	10.30 [36]	1.47 [20]	5.12 [39]	5.20 [20]
»	Ph_3AsO	1.66[a] [32]	880 [1]	5.82 [38,30]	—	5.53 [40]	5.27 [20]
»	Ph_3AsO	1.64 [33]	885 [29]	6.01 [20]	—	—	5.84 [40]
Arsinic acids	$Me_2As(O)OH$	1.61[b] (1.63) [34]	869 [31]	5.77 [31]	1.43 [31]	—	—
Arsonic acids	$MeAs(O)(OH)_2$	1.65[b] (1.75) [34]	913 [31]	6.39 [31]	1.54 [31]	—	—
Arsinate esters	$Me_2As(O)OMe$	1.64[c] (1.78) [24]	929 [24]	6.51 [24]	1.61 [20]	4.00[d] [20]	3.80[d] [20]
		—	—	6.71 [20]	—	—	—
Arsonate esters	$MeAs(O)(OMe)_2$	1.62[c] (1.78) [24]	954 [24]	6.91 [24]	1.67 [20]	2.88 [20]	3.20 [26]
		—	—	7.01 [20]	—	—	—
Arsonates	$(MeO)_3AsO$	1.61[c] (1.78) [24]	975 [24]	7.38 [20]	1.74 [20]	3.08[e] [20]	2,45 [26,20]
		—	976 [36,37]	7.24 [24]	—	—	— —
		—	—	12.00 [36]	—	—	— —

Remarks: *a*) monohydrate; *b*) the bond lengths r(As=O) and r(As–O) may become equalised as a result of the involvement of the oxygen of the arsenyl bond in a hydrogen bond[34]; *c*) calculated values; *d*) for $Bu_2As(O)OBu$; *e*) for $(EtO)_3AsO$; *f*) for $PhAs(O)(OH)_2$.

Note. Here and in the other tables the numbers in square brackets denote references (Ed.of Translation).

†By analogy with the phosphoryl bond P=O, the term arsenyl bond for As=O is more useful than another term sometimes encountered in the literature.

II. THE NATURE OF THE ARSENYL BOND

The nature of the arsenyl bond has been discussed in numerous studies[19,20,24-30]. All the investigators have concluded that the arsenyl bond is complex and differs from covalent, single, and double bonds and at the same time is not a purely semipolar bond. Certain physical characteristics of the arsenyl bond are listed in Table 1.

Comparison of the As=O and As–O bond lengths shows that the difference between them (up to 0.1 Å) is much smaller than the difference between the sums of the radii of As and O atoms involved in single and double bonds (0.17 Å).[34] Calculation of the lengths of formally double and single bonds, r(As=O) and r(As–O), from the Schomaker-Stevenson formula yields 1.58 and 1.74 Å respectively[29]. Table 1 shows that the experimental value of r(As=O) differs from the above values. Unfortunately the experimental values of r(As=O) refer to the arsenyl group whose oxygen atom is involved in a hydrogen bond.

It has proved convenient to investigate arsenyl compounds by vibrational spectroscopic methods, particularly by infrared spectroscopy[20,24,29,30,35,36,37,41-50]. It has been established that the vibration which is characteristic not only as regards frequency but also as regards mode, corresponds to the arsenyl group in the infrared spectrum. The As=O stretching vibration makes a contribution greater than 95% to the band assigned to the vibration of this bond, while in the case of the As–O bond there is no rigorously characteristic vibration[20,24,36]. Calculations of the stretching vibration frequencies ν(As–O) and ν(As=O) yielded 670 and 1010 cm^{-1}.[29] The calculated and experimental data for the arsenic–oxygen single bond are similar; ν(As=O) is active in the range 600–748 cm^{-1}.[29,50]. The regions where ν(As=O) is active for different derivatives of tetracoordinate arsenic are given in Table 2. Evidently ν(As=O) is active in the range 845–980 cm^{-1} and the experimental values thus differ from the values calculated for the double bond. The influence of substituents on the spectral characteristics of the As=O bond are as a rule additive, as for P=O.[44] A linear relation has been discovered between ν(As=O) and the sum of the constants χ of the substituents at the arsenic atom[29]: $\nu(As=O) = 720 + 30\Sigma\chi$, where χ are the substituent constants (the "group electronegativities" of the substituents derived for phosphoryl compounds). There is a similar relation also for the P=O bond[64]: $\nu(P=O) = 930 + 40\Sigma\chi$.

Such additivity shows that the phosphoryl and arsenyl groups are not directly involved in the resonance interaction with the substituents at the phosphorus and arsenic atoms, which does not, however, rule out the probability of a specific interaction of certain substituents with phosphorus and arsenic atoms[44]. Thus, for "narrow" series, for example, for *para*-substituted phenyl phosphonates and dialkylarylarsine oxides, p-$XC_6H_4P(O)(OEt)_2$ and p-XC_6H_4.$As(O)Et_2$, a linear relation has been found between ν(P=O) and ν(As=O), on the one hand, and the Hammett constants for *para*-substituents, on the other[42]: $\nu(As=O) = 904 + 5\sigma$, $r = 0.98$; $\nu(P=O) = 1260 + 9\sigma$, $r = 0.92$. Since the Hammett constants include a resonance component, the existence of such relations can be treated as evidence for the conjugation of the substituents with the phosphorus and arsenic atoms. Shagidullin[42,44] arrived at the same conclusion in the analysis of ultraviolet spectroscopic data. Analysis of the M=X vibrational frequencies in compounds of the type $R_3M=X$, where M=P, As, or Sb, X=O, S, Se, or Te, and R are alkyl groups, showed[35], that, for identical R, the frequency ν(M=X) depends on the mass of the molecule and the electronegativities of the M and X atoms:

$$\nu_{M=X} = k\left[\frac{\Sigma M}{(m_M\ m_X)}\right]^{1/2} E_M E_X,$$

where M is the mass of the molecule, m the mass of the given atom, and E the electronegativity of the atom.

The differences between the stretching vibration frequencies ν(As=O) in the spectra of various compounds of tetracoordinate arsenic, the differences between the force constants of the As=O bond, and calculations of the order of this bond based on infrared spectroscopic data (Tables 1 and 2) showed, that, depending on the environment of the arsenic atom, the bond multiplicity N varies from 1.4 to approximately 1.8 $N \cong 1.5$ for arsine oxides, $k_{P=O} = 8.25$ and $N \cong 1.9$ for the oxide Me_3PO, and $k_{N\to O} = 3.90$ and $N = 0.65$ for Me_3NO.[30] Many investigators explain such differences in the multiplicities of the NO, PO, and AsO bonds on the basis of the concept of vacant d orbitals[19,20,30,55,56]. Although the NO bond in amine oxides can be regarded as the semipolar $(CH_3)_3\overset{+}{N}-O^-$ linkage, nevertheless calculations of the electronic structures of the compounds X_3NO have shown that there is some displacement of the electrons of the oxygen atom to the nitrogen atom: $p_\pi(O) \to p_\pi(N)$.[56] In phosphorus and arsenic compounds there is a possibility of p_π–d_π interaction between the vacant

Table 2. The regions where the ν(As=O) stretching vibrations are active in the infrared spectra of compounds of tetracoordinate arsenic.

Compound	R_3AsOH ‖ O	RAs(OH)$_2$ ‖ O	R_3AsO	R_3AsOR' ‖ O	RAs(OR′)(NR″$_2$) ‖ O	RAs(OR′)$_2$ ‖ O	(RO)$_2$AsNR′$_2$ ‖ O	(RO)$_3$AsO
$\nu_{As=O}$, cm^{-1}	870 [22]	845–940 [31,51]	880–910 [35,41]	920–930 [48,49]	940–950 [52]	950–960 [29,43]	940–960 [53]	955–978 [24,50]

2*p* orbitals of oxygen and the corresponding 3*d* and 4*d* orbitals of the heteroatoms, which leads to an increase of the multiplicity of the phosphoryl and arsenyl bonds. Since $2p_\pi-3d_\pi$ interaction is energetically more favourable than the $2p_\pi-4d_\pi$ interaction, the above interaction plays a more important role in the phosphorus compounds and leads to a greater increase in the multiplicity of the P=O bond.

This situation has also been confirmed by the dissociation energies of the E=O bonds. The dissociation energy of the arsenyl bond has been determined from thermochemical data for the oxides As_4O_{10} [57] and Ph_3AsO.[58] For comparison, Table 3 presents the dissociation energies of the element–oxygen bonds. It is seen from these data that the dissociation energy of the phosphoryl bond is much higher than for other E=O bonds (cf. also the dissociation energies of the N→O and P=O bonds in F_3NO and F_3PO, which are 410 and 540 kJ mol^{-1} respectively[69]). The difference between the dissociation energies of single element–oxygen bonds is much smaller. If the difference between the dissociation energies of single and double bonds is assumed to be, after Mitchell[55], the contribution of the π-component to the formation of the E=O bond, then, according to the data in Table 3, this contribution is 217–301 kJ mol^{-1} (159 kJ mol^{-1} according to Mitchell[55]) for phosphorus and 88–142 kJ mol^{-1} for arsenic. In the carbonyl group the contribution of the π-component is much greater, amounting to 335–377 kJ mol^{-1}, which can be explained by certain factors, including the shorter length of the CO bond and the more effective $p_\pi-p_\pi$ overlap[55].

Table 3. The element–oxygen bond dissociation energies.

Compound	Bond	Bond energy, kJ mol^{-1}	Compound	Bond	Bond energy, kJ mol^{-1}	Compound	Bond	Bond energy, kJ mol^{-1}
E_4O_6 [57]	P—O	335	E_4O_{10} [57]	P=O	653	Ph_3EO [58]	P=O	552
»	As—O	301	»	As=O	389	»	As=O	443
»	Sb—O	297	»	Sb=O	399	»	Sb=O	439

Measurements of the dipole moments of compounds of tetracoordinate arsenic and calculations of the dipole moments of the As=O bond (see Table 1) indicate a high polarity of this bond. The relative polarity of the As=O bond in tertiary arsine oxides is higher than that of the As=S bond in the analogous sulphides, which can be accounted for by two factors: the stronger $p_\pi-d_\pi$ interaction between the sulphur and arsenic atoms and the smaller charge separation in the σ-bond as a consequence of the lower electronegativity of the sulphur atom[59].

Comparison of the dipole moments of the arsenyl and phosphoryl bonds (Tables 4 and 1) shows that higher values are characteristic of the As=O bond in the analogous compounds and that the difference Δμ increases with the number of electronegative substituents linked to the heteroatom.

The influence of the arsenyl group is reflected in the ^{1}H NMR spectra by a downfield shift of the proton signals of the substituents linked to the arsenic atom[20,25,26,62]. An analogous effect has also been observed for substituents linked to the phosphoryl group[63]. The arsenyl bond exerts a deshielding influence on both methyl and methylene protons (a displacement of the signals by 0.55–0.75 p.p.m.) and on phenyl protons (a displacement by approximately 0.35 p.p.m.). The regions where the proton-containing groups linked to the heteroatom in the tervalent state are manifested correspond to the electronegativities of the heteroatoms of[20] and are similar for arsenic and phosphorus compounds (Table 5). An increase of coordination number from three to four causes an appreciable alteration of the chemical shifts (Δδ, Table 5) for arsenic and phosphorus compounds and, as for the dipole moments (Δμ, Table 4), the difference increases with increase of the number of electronegative substituents (from 0.13 to 0.64 p.p.m.).

Table 4. Comparison of the dipole moments of the phosphoryl and arsenyl bonds: $\Delta\mu = \mu_{As=O} - \mu_{P=O}$.

Compound	$\mu_{P=O}$, D		Δμ, D
Me_3EO	4.3	[60,61]	0.9
$R_2(RO)EO$	1.6	[61]	2.2
$(RO)_3EO$	0.2	[61]	2.3

The increase can be accounted for in terms of the increasing role of $p_\pi-d_\pi$ interaction for phosphorus compounds with increase of the number of electronegative substituents at the phosphorus atom. It is known that, with increase of the positive charge on the atom (P or S), its 3*d* orbitals contract and favourable conditions are created for the overlap with the 2*p* orbitals of oxygen[64,65] (an increase in the multiplicity of the phosphoryl bond leads to a decrease of the dipole moment and of electron-attracting character in the bond to proton-containing substituents).

Table 5. The chemical shifts of the proton-containing groups linked to heteroatoms[20].

Compound	δ_{E-Me} (δ_{E-CH_2}), p.p.m.	Δδ*, p.p.m.	Compound	δ_{E-Me} (δ_{E-CH_2}), p.p.m.	Δδ*, p.p.m.
Me_3As	0.94	—	Me_3NO	3.32	−1.63
Me_3P	0.98	−0.04	Et_3AsO	1.31 (2.01)	—
Me_3N	2.1	−1.06	Et_3PO	1.16 (1.71)	—
$Me_2(MeO)As$	1.20	—	Et_3NO	1.31 (3.24)	—
$Me_2(MeO)P$	1.23	−0.03	$Me_2(MeO)AsO$	1.77	—
$Me(MeO)_2As$	1.19	—	$Me_2(MeO)PO$	1.40	0.37
$Me(MeO)_2P$	1.16	0.03	$Me(MeO)_2AsO$	2.00	—
Me_3AsO	1.69	—	$Me(MeO)_2PO$	1.36	0.64
Me_3PO	1.56	0.13			

*$\Delta\delta = \delta_{As-Me} - \delta_{E-Me}$.

If $\Delta'\delta = \delta_{OEMe} - \delta_{EMe}$ is adopted as characteristic of the change in the charge on the heteroatom, then the charge for different E varies in the sequence N > As > P ($\Delta'\delta$ = 1.2, 0.75, and 0.58 p.p.m. respectively).

X-Ray electronic spectroscopy appears to be extremely promising for the estimation of effective atomic charges in compounds and of the donor-accepter capacity of the ligands[66]. X-Ray spectroscopic methods have been used to investigate the $R_2S-R_2SO-R_2SO_2$ and $R_3NO-R_3PO-R_3AsO$ series[67,68]. X-Ray emission spectra of the sulphur atoms in Me_2SO and Me_2S indicate partial population of the 3*d*

orbital of the sulphur atom in the oxide as a result of $p_\pi-d_\pi$ interaction. The X-ray spectra of the oxygen in R_3EO (E = N, P, or As) also reveal $p_\pi-d_\pi$ interaction in R_3PO. The available data for R_3NO and R_3AsO are insufficient to rule out completely the occurrence of π-bonding in these compounds, but one may conclude that, even if it does occur, it is much weaker than in R_3PO.[67] The determination of the energy of the 1s level of oxygen in the compounds $(C_8H_{17})_3NO$, $(iso\text{-}C_5H_{11})_3PO$, and $(C_8H_{17})_3AsO$ yielded $E(O1s) = 531.3$, 532.2, and 530.0 eV respectively[68]. The energy of the 1s level of oxygen in R_3PO is a maximum, i.e. the negative charge on the oxygen atom in phosphine oxides is a minimum, the value of $E(O1s)$ in phosphine oxides and sulphoxides being similar [$E(O1s)$ = 532.1 eV for R_2SO].[68]

Summarising the investigations of the arsenyl bond, one must conclude that the nature of the arsenyl linkage can be represented by several structures differing in their multiplicity:

$$R_3\overset{\oplus}{As}-\overset{\ominus}{O} \leftrightarrow R_3\overset{\delta+}{As} \cdots \overset{\delta-}{O} \leftrightarrow R_3As{=}O.$$

The multiplicity is influenced by the nature of the substituents linked to the arsenic atom: electron-donating substituents decrease the multiplicity (a semipolar bond), while electron-accepting substituents increase it.

Problems associated with the nature of the arsenyl bond will also be considered in Section III in connection with the basicities of tertiary arsine oxides in water[70] and nitromethane[71]. Proton-containing solvents, including water, reduce the charge on the oxygen atom as a result of the formation of hydrogen bonds with the oxygen of the arsenyl group. In contrast to the behaviour in nitromethane, tertiary arsine oxides are therefore weak bases in water whose pK_a are independent of the length of the hydrocarbon group attached to the arsenic atom[70] (the levelling influence of water).

Thus the arsenyl bond is a complex labile linkage, which varies from a semipolar to a partially multiple bond.

III. THE BASICITY AND PROTON-ACCEPTING CAPACITY OF ARSENYL COMPOUNDS IN THE FORMATION OF HYDROGEN BONDS

The ability of the arsenyl group to participate in complex formation with metal salts, hydrogen bonding, and acid-base interactions is the most important and most characteristic property of arsenyl compounds. The question of the possible classification of all these interactions of the donor–acceptor type and the role of charge transfer in these processes are controversial[72–75]. However, it has come to be assumed that the complexes of oxygen-containing extractants R_nEO with metal salts are formed via the mechanism of electron donor–electron acceptor interactions (EDA).[76] The classification of hydrogen-bonded complexes as EDA complexes has also been receiving increasing recognition[73,74]. Bent's view[77] that the formation of a hydrogen bond is the first stage in acid–base reactions with proton transfer has also been widely accepted[74,75].

Although there exists a view[73] that the pK_a cannot serve as a reliable measure of the electron-donating and electron-accepting molecules, nevertheless the basicity of compounds of the type R_nEO (E = N, P, As, S, or Se), which we shall call for brevity oxa-bases, is at present the best characteristic of the electron-donating capacity of oxygen, since the extracting capacity of these compounds varies in parallel with their basicity[67,75]. It has been shown[75] that the parameters characterising the hydrogen bond should characterise more adequately than the basicity (pK_a) the distribution of electron-density in the molecule in the ground state.

The constants characterising basicity and proton-accepting capacity in the formation of hydrogen bonds are thermodynamic data and cannot yield direct information about reaction mechanisms, but they do have a great advantage over kinetic data, because they can be used directly to compare the structures of the compounds[78].

Numerous studies have been devoted to the determination of the basicities of arsenyl compounds and other oxa-bases, but comparison of the pK_a obtained by different groups of investigators is difficult because of the lack of generally accepted standard methods; this applies particularly to titration in non-aqueous media. When arsenyl compounds are titrated, quaternary arsonium salts are formed ($R_3AsO + H^+ \rightarrow R_3AsOH^+$) and, although the arsenic atom is not involved in the protonation process, the multiplicity of the arsenic–oxygen bond changes[79].

The basicity of derivatives of tetracoordinate arsenic depends on the electronic effects of the substituents at the arsenic atom, which is also a consequence of the lability of the arsenyl bond. Different derivatives of tetracoordinate arsenic give rise to the following series based on the variation of basicity[71]:

$$RAs\begin{matrix}OR' \\ \| \\ O \\ NR''_2\end{matrix} > R_3AsO > R_2As(O)OR' \geqslant R_2As(O)OH >$$
$$> RAs(O)(OR')_2 \geqslant RAs(O)(OH)_2 > (RO)_3AsO \quad .$$

In this series the high basicity of the amidoesters of arsonic acids is due to the protonation of the nitrogen atom of the amido-group[71,78] and does not therefore indicate a high polarity of the arsenyl bond in these compounds.

Numerous correlation equations have now been found for the relation between the pK_a for the arsenyl compounds and the substituent constants σ, σ^+, σ^-,[81] σ^*, σ_I^{Ph}, and σ^{Ph} [49,71,82,83]. The use of σρ-analysis for organoarsenic compounds has been surveyed in a review[79] whose authors concluded that mainly the inductive effects of the substituents are transmitted via the arsenic atom.

The basicities of arsine sulphides and selenides are very much lower than those of arsine oxides[82,84], which, as mentioned above, corresponds to lower polarities of the As = S and As = Se bonds compared with As = O.

The comparison of the basicities and proton-accepting capacities in the formation of hydrogen bonds in the oxa-bases of Group VA and VIA elements incorporating similar functional groups E = O (E → O), responsible for the above properties of these compounds, is of very great interest. In contrast to non-oxidised compounds, examination of the oxa-bases of Group VA and VIA elements makes it possible to eliminate the influence of steric factors from the comparison. Thus analysis of numerous literature data on intermolecular hydrogen bonding involving compounds of Group VA and VIA elements shows that in the compounds R_2EO and R_3EO the influence of steric effects of the substituents is virtually absent, while in the compounds R_2E and R_3E it is large[85].

Hitherto mainly the problem of the involvement of compounds of the type R_2E and R_3E, where E are Group VA and VIA elements, in the formation of hydrogen bonds and acid–base interactions has been discussed in the literature[72,78,86,90]. It has been discovered for a large number of examples that the electron-donating capacities of the compounds R_2E and R_3E, where R is an alkyl substituent, diminish on passing to heavy elements: N > P > As > Sb and

O > S > Se > Te, the greatest differences being observed on passing from elements of the Second Period to those of the Third Period—from nitrogen to phosphorus and from oxygen to sulphur. Within any Period, for example, with increase of the number of the Group, the electron-donating capacity falls: N > O > F; P > S > Cl; As > Se > Br; Sb > Te > I. On passing to aromatic derivatives (R = Ar), complexes involving the π-system of the benzene ring as the proton acceptor appear; in this case there is a possibility of an inversion of the series based on the variation of the electron-donating capacity[86]. Thus the electron-donating capacity within a single Period decreases with increasing electronegativity of the heteroatoms, while within a single Group the electron-donating capacity increases as the electronegativity of the heteroatom increases; this gives rise to difficulties in the analysis of factors determining the electron-donating capacity of compounds.

The direction in which the electron-donating capacity changes within a single Period can be accounted for simply and logically—an increase of the electronegativity of the heteroatom leads to a greater difficulty of the abstraction of valence electrons; this is consistent with the increase of the ionisation potential and with decrease of the electron-donating capacity of the elements[78].

According to modern ideas, the electron-donating capacity of compounds is determined by two factors: the charge transfer from the *np* orbital of the atom E to the antibonding σ orbital of the A–H bond of the proton donor and the overlap of the 1s orbitals of the H atom with the *n* orbitals of the electron donor[72,86]. The increase of I hinders the charge transfer, which entails a decrease of the electron-donating capacity[72]. Since the ability of the orbitals to overlap decreases with increasing diffuseness of the orbitals of the donor *n* electrons, i.e. with increase of the principal quantum number *K*, the influence of the overlap within a single Period can be regarded as constant[86]. Within a single Group, an increase of the atomic number of the element entails a decrease of *I* and an increase of *K*, i.e. both factors (charge transfer and the overlap of the orbitals) exert an influence on the electron-donating capacity of the elements and there is a possibility of partial or complete cancelling of these effects[86].

The data for the basicities of the oxa-bases of Group VA and VIA element of the type R_nEO are presented below.

(1) Acid—H_2SO_4, comparison parameter—pK_a, solvent—water[87]:

$$\underset{4.65}{Me_3NO} > \underset{3.75}{Me_3AsO} > \underset{0.9}{Me_2SO} > \underset{-3.2}{Ph_2MePO} > \underset{-6.15}{PhMeCO}\ .$$

The basicity increases in the sequence N > As > P.

(2) Acid—$HClO_4$, comparison parameter—pK_a, solvent—water[88]:

$$\underset{2.55}{Me_2SeO} > \underset{1.02}{C_5H_5Me_2NO} > \underset{1.01}{Ph_3AsO} > \underset{0.79}{C_5H_5NO} > \underset{0.54}{Ph_2SeO} > \underset{-2.10}{Ph_3PO} > \underset{-2.03}{(PhCH_2)_2SO} > \underset{-3.19}{Ph_2SO}$$

or $Ph_3AsO > C_5H_5NO > Ph_2SeO > Ph_3PO > Ph_2SO$. The basicity decreases in the sequences As > N > P, Se > S, As > Se, and P > S.

(3) Acid—$HClO_4$, comparison parameter—ionisation constant K_i, solvent—acetic acid[88]:

$$\underset{4.60\cdot10^6}{Ph_3AsO} > \underset{2.73\cdot10^6}{C_5H_5Me_2NO} > \underset{4.18\cdot10^5}{Ph_2SeO} > \underset{2.82\cdot10^5}{C_5H_5NO} > \underset{2.72\cdot10^2}{Ph_2PO} > \underset{9.34}{Ph_2SO};\ \underset{10^8}{Me_2SeO} > \underset{3.44\cdot10^3}{Me_3PO} > \underset{3.50\cdot10^2}{Me_2SO}\ .$$

The basicity decreases in the sequences As > N > P, Se > S, As > Se, and P > S.

(4) Comparison parameter—pK_a, solvent—water#:[89]

$$\underset{6}{Me_2TeO} > \underset{5.36}{Me_3SbO} > \underset{4.65}{Me_3NO} > \underset{3.75}{Me_3AsO} > \underset{2.55}{Me_2SeO} > \underset{0}{Me_3PO} \simeq \underset{0}{Me_2SO}\ .$$

The basicity decreases in the sequences Sb > N > As > P, Te > Se > S, Te > Sb, and As > Se.

(5) Acid—$HClO_4$, comparison parameter—pK_a, solvent—nitromethane[84]:

$$\underset{12.76}{Ph_3SbO} \geqslant \underset{12.58}{Ph_3AsO};\ \underset{16.58}{Oct_3SbO} > \underset{16.18}{Oct_3AsO}\ .$$

The basicity decreases in the sequence Sb > As.

Data for the proton-accepting capacities in the formation of hydrogen bonds by the oxa-bases of Group VA and VIA elements of the type R_nEO are presented below.

(1) Proton donor—HSCN, comparison parameter—Δν, solvent—CCl_4:[88]

$$Oct_3PO > Me_3PO > Ph_3PO > Me_2SO > (PhCH_2)_2SO > Ph_2SO\ .$$

The proton-accepting capacity decreases in the sequence P > S.

(2) Proton donor—PhOD, comparison parameter—Δν, solvent—CCl_4:[88]

$$Ph_3AsO > Me_2SeO > C_5H_3(Me)_2NO > Oct_3PO \geqslant Me_3PO > C_5H_5NO > Ph_3PO > Me_2SO > (PhCH_2)_2SO > Ph_2SO\ .$$

The proton-accepting capacity decreases in the sequences As > N > P, Se > S, and P > S.

(3) Proton donor—methanol, comparison parameter—Δν, solvent—CCl_4:[88]

$$Ph_3AsO > Me_2SeO > C_5H_3(Me)_2NO \simeq Oct_3PO > C_2H_5NO > Me_3PO > Ph_2SeO > Ph_3PO > (PhCH_2)_2SO > Ph_2SO\ .$$

The proton-accepting capacity decreases in the sequences As > N > P, Se > S, As > Se, and P > S.

(4) Proton donor—indole, comparison parameter—Δν, solvent—CCl_4:[88]

$$Ph_3AsO > Me_2SeO > Oct_3PO > C_2H_5NO > Me_3PO > Ph_2SeO > Ph_3PO > C_5H_3(Me)_2NO > Me_2SO > (PhCH_2)_2SO > Ph_2SO.$$

The proton-accepting capacity decreases in the sequences As > N > P, Se > S, As > Se, and P > S.

(5) Proton donor—PhN(Me)H, comparison parameter—Δν, solvent—CCl_4:[88]

$$Ph_3AsO > Me_2SeO > Oct_3PO > C_5H_5NO > Me_3PO > C_5H_3(Me)_2NO \simeq Ph_2SeO \simeq Ph_3PO > Me_2SO > (PhCH_2)_2SO > Ph_2SO\ .$$

The proton-accepting capacity decreases in the sequences As > N > P, Se > S, As > Se, and P > S.

(6) Proton donor—HOOCPhX (X = 3-NO_2, 4-NO_2, or 3-Cl), comparison parameter—Δν, crystalline adducts[91]:

$$Ph_3AsO \simeq C_5H_5NO > Ph_3PO\ .$$

The proton-accepting capacity decreases in the sequence As ≅ N > P.

(7) Proton donor—phenol, comparison parameters—Δν, ΔH, and K_d^{298}, solvent—CCl_4:[92,93]:

$$R_3AsO > R_3PO;\ Oct_3AsO > Bu_3AsO > Ph_3AsO\ .$$

The proton-accepting capacity decreases in the sequence As > P.

(8) Donors—Ph_3COH and Ph_3COD, comparison parameters—Δν, crystalline adducts[94]:

$$Ph_3AsO > Ph_2SeO > Ph_2SO\ .$$

#The salts, for example, $R_nEO.HNO_3$, were titrated with alkali[89].

The proton-accepting capacity decreases in the sequences Se > S and As > Se.

(9) Proton donor—water, comparison parameter—$K_{298°}$, solvent—CCl_4:[95,96]

$$Alk_3AsO > Alk_3PO;\ Oct_3AsO > Ph(Oct)_2AsO > Bu_3AsO > Ph_2(Oct)AsO > Et_3AsO\ .$$

The proton-accepting capacity decreases in the sequence As > P.

(10) Proton donor—water, comparison parameters—$\Delta\nu$, E_H, and $\overline{K}$, solvent—CCl_4:[67]

$$Oct_3NO \simeq Oct_3AsO > iso\text{-}Am_3PO > Oct_2SO > (BuO)_3PO\ .$$

The proton-accepting capacity decreases in the sequences N ≅ As > P and P > S.

(11) Proton donor—CF_3COOH, comparison parameter—ΔH, solvent—CCl_4:[97]

$$Oct_3NO > Oct_3AsO > C_5H_5NO > Me(Bu)_2PO > Me_2SO > (BuO_3)PO\ .$$

The proton-accepting capacity decreases in the sequence N > As > P > S.

(12) Proton donor—CF_3COOH, comparison parameter—ΔH, solvent—benzene[98]:

$$Et_3AsO > Ph_3AsO > Et_3AsS\ .$$

(13) Proton donor—CCl_3COOH, comparison parameter—ΔH, solvent—CCl_4:[97]

$$Oct_3AsO > C_5H_5NO > Oct_3PO > (C_6H_{13})_2SO\ .$$

The proton-accepting capacity decreases in the sequence As > P > S.

(14) Proton donor—4-FC_6H_4OH, comparison parameter—ΔH, solvent—CCl_4:[99,100]

$$Me_3NO > Me_3PO \simeq C_5H_5NO > Me_2SO\ .$$

The proton-accepting capacity decreases in the sequence N > P > S.

(15) Proton donor—$CH_2ClCOOH$, comparison parameter—ΔH, solvent—CCl_4:[101]

$$Oct_3PO > Ph_2SeO > Ph_3PO > Me_2SO > Ph_2SO\ .$$

The proton-accepting capacity decreases in the sequences P > S and Se > S.

(16) Proton donor—$CHCl_2COOH$, comparison parameter—ΔH, solvent—CCl_4:[101]

$$Oct_3PO > Ph_2SeO > Ph_3PO > Me_2SO > Ph_2SO\ .$$

The proton-accepting capacity decreases in the sequences P > S and Se > S.

(17) Proton donor—PhC ≡ CH, comparison parameter—$\Delta\nu$, solvent—CCl_4:[88]

$$Ph_3AsO > Me_2SeO > Oct_3PO > Ph_2SeO > C_5H_3(Me)_2NO \simeq \simeq Me_3PO > Ph_3PO > C_5H_5NO \geq Et_2SO \geq Me_2SO > Ph_2SO\ .$$

The proton-accepting capacity decreases in the sequences As > P > N, Se > S, As > Se, and P > S.

Evidently the sequences in which the basicity (pK_a) and the parameters characterising the hydrogen bond ($\Delta\nu$, ΔH, K, and E_H) vary are in most cases the same. It has been stated[88] that a simple relation between the pK_a and the parameters characterising the hydrogen bond holds for strong proton donors. For weak proton donors (for example, phenylacetylene), the pK_a and the parameters characterising the hydrogen bond do not always vary in parallel. Since the main bulk of the available experimental data on the involvement of the oxa-bases R_nEO in hydrogen bonding refer to strong proton donors, i.e., according to the classification adopted by Sergeev[102], these are moderately strong and strong hydrogen bonds, we observe a correspondence between the degree of protonation (i.e. the pK_a) and hydrogen bonding (i.e. $\Delta\nu$, ΔH, K, and E_H).

It is known that charge transfer from the donor to the acceptor molecule assumes an appreciable role in the formation of hydrogen-bonded complexes with strong and moderately strong hydrogen bonds[73,104]; on this basis, the above hydrogen-bonded complexes have been included in the general system for the classification of charge-transfer complexes, i.e. they can be regarded as EDA complexes.

The observed correspondence between the parameters characterising the basicity (pK_a) and the hydrogen bond ($\Delta\nu$, ΔH, E_H, and K) shows that these quantities characterise reliably the electron-donating capacity of the oxa-bases. The possibility of a correlation between the parameters of the hydrogen-bonded complexes and the pK_a has been questioned[73]. It was stated that such correspondence can refer only to a narrow range of analogous complexes, where the acid–base interaction proceeds up to the formation of solvated ions. Evidently, the oxa-bases, which are weak acceptors in ionisation (they are protonated in media with a high acidity[103]) and strong acceptors in hydrogen bonding[88], are precisely the type of compounds whose protonation leads to the formation of solvated ions.

It follows from the data presented that the electron-donating capacity of aliphatic derivatives Alk_nEO is always greater than that of aromatic derivatives Ar_nEO and that the replacement of alkyl groups by alkoxy-groups also entails a decrease of the electron-donating capacity of the oxa-bases. Comparison of the oxa-bases with substituents of the same type is therefore legitimate for the detection of the influence of E on the electron-donating capacity.

Analysis of the data presented permits the following conclusions. The first conclusion is the same as that reached in the analysis of the properties of the oxygen-free bases R_nE formed by Group VA–VIIIA-elements[72,78,86]: within any Period, the electron-donating capacity of the oxa-bases R_nEO decreases with increase of the number of the Group regardless of the Period under consideration. In all cases the basicity and proton-accepting capacity of phosphine oxides are greater than those of the sulphoxides and those of arsine oxides are greater than those of selenoxides. According to Nylen[89], the only exception is that Me_2TeO is somewhat more basic than Me_3SbO, but this requires an experimental test, since the author himself[89] believes that the pK_a for Me_2TeO has been determined only approximately.

There is a non-monotonic variation of the electron-donating capacities of the oxa-bases R_nEO within a single Group—the oxa-bases of the Second and Fourth Periods are stronger electron-donors than the oxa-bases of the Third Period (always $R_3NO > R_3PO$, $R_3AsO > R_3PO$, and $R_2SeO > R_2SO$); the oxa-bases of the Fifth Period are stronger electron donors than those of the Fourth Period ($R_3SbO \gtrsim R_3AsO$ and $R_2TeO > R_2SeO$).

Thus the following series based on the variation of the electron-donating capacities of the oxa-bases can be set up within Groups VA and VIA: Sb > As > P < N or Sb > As ≅ N > P and Te > Se > S. We may note that the electron-donating capacities of arsine and amine oxides are similar, so that, according to the data presented above, they frequently change places (this finding is also evidence in support of the semipolar nature of the arsenyl bond in arsine oxides). Consequently, partial inversion of the series based on the variation of the electron-donating capacity found for the non-oxidised bases R_nE has been observed for the oxa-bases R_nEO: N > P > As > Sb and O > S > Se > Te.[72,78]

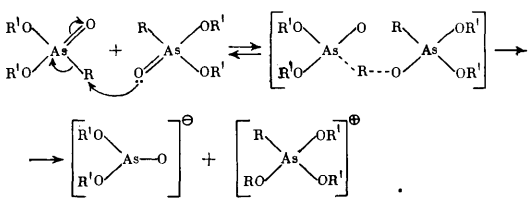
The observed characteristics of the variation of the electron-donating capacities of the oxa-bases R_nEO, where E are Group VA and VIA elements, on the whole agree with the known type of variation of the electronegativities and

the ionisation potentials *I* of these elements: with increase of the number of the Group and with decrease of the atomic number of the element within the Group (i.e. from left to right and from below upwards in the Periodic System), the electronegativity and *I* increase, which should naturally entail a decrease of the electron-donating capacity. The nitrogen atom is an exception in this instance.

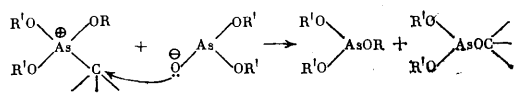
As stated above, the overlap of the 1*s* orbitals of the hydrogen atom with the *n* orbitals of the donor plays an appreciable role in the formation of hydrogen bonds in addition to the charge transfer from the *np* orbital of the donor to the antibonding orbital of the A–H acceptor. When the oxa-bases R_nEO are involved in the formation of hydrogen bonds, the 1*s* orbitals of hydrogen always overlap with the *n* orbitals of oxygen, i.e. the second factor may be regarded as constant. The influence of E on the electron-donating properties of the oxa-bases, which is transmitted via the oxygen atom, evidently reduces to an influence on the charge transfer from the oxygen atom (donor) to the acceptor molecule.

IV. THE NUCLEOPHILIC PROPERTIES OF ARSENYL COMPOUNDS

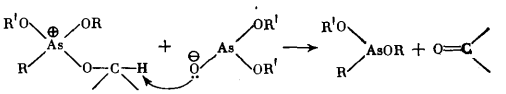
Many reactions are now known in which the nucleophilic properties of arsenyl compounds in relation not only to the proton but also to the carbon atom are manifested. An example of such reactions is the thermal transformations of arsonic and arsinic acids and arsine oxides. The mechanisms of these fairly complex reactions have been analysed in detail[19]. The pyrolysis of arsenyl compounds apparently begins with the nucleophilic attack by the oxygen of the arsenyl Group on the α-carbon atom attached to the arsenic atom:



Further attack by the anion on the α-carbon atom of the cation leads to isomerisation products:

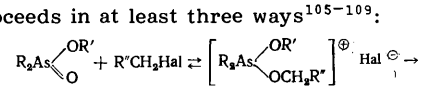


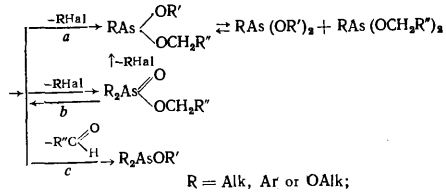
while the reaction involving the hydrogen at the α-carbon atom of the cation leads to the formation of reduction products and aldehydes:



Isomerisation predominates for arsonic acid esters, while reduction predominates for arsine oxides[19].

Together with thermal transformations, the interaction of arsenyl compounds with electrophiles has been studied. The interaction of arsonic and arsinic acid esters with alkyl halides proceeds in at least three ways[105–109]:





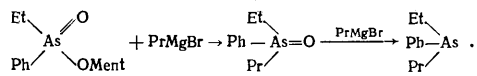
(1)

R = Alk, Ar or OAlk;
R′ = Alk; R″ = Alk or Ar .

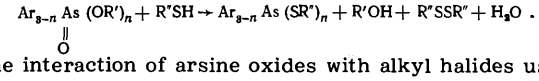
Nucleophilic attack by the oxygen of the arsenyl group on the α-carbon atom of the alkyl halide leads to the formation of an alkoxyarsonium salt, further reactions of which are determined by the nature of the reactants and the reaction conditions. In the presence of an aliphatic carbon atom linked to arsenic (alkylarsonic and dialkylarsinic acid esters) the attack by the nucleophile is directed to the α-carbon atom of the alkoxyarsonium cation; as a result, a retro-Arbuzov rearrangement of the initial esters takes place (pathway *a*) with formation of a new alkyl halide. The esters of alkyl alkylarsonous and arsenous acids formed under these conditions are usually symmetrised. If the alkyl halide produced in this reaction (RHal) is more reactive than the initial halide ($R''CH_2Hal$), then RHal will subsequently participate in the reaction preferentially and isomerisation products will predominate among the reaction products.

Pathway *b*, i.e. attack by the nucleophile on the α-carbon atom of the calkoxy-group of the alkoxyarsonium cation as a result of which the arsenyl group is regenerated, is characteristic of aromatic derivatives (esters of arylarsonic and diarylarsinic acids). The pathway in which the nucleophile abstracts a proton from the α-carbon atom of the alkoxy-group (α-elimination), which results in the formation of an aldehyde and the product of the reduction of the initial ester, obtains for the same compounds under more severe conditions (on increase of reaction temperature to 180–195 °C).

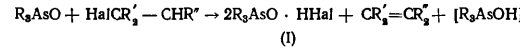
The menthyl esters of alkylarylarsinic acids react with alkylmagnesium halides with inversion of the configuration and for a molar reactant ratio of 1 : 1 a tertiary arsine oxide is formed, while for a ratio of 1 : 2 reduction to the corresponding arsine takes place[110]:



The reduction of quinquevalent arsenic acid esters is also observed in their reactions with mercaptans, which entails an exchange of the alkoxy-group of the ester for the mercapto-group[111]:



The interaction of arsine oxides with alkyl halides usually leads to the dehydrohalogenation of the alkyl halide by the oxide with formation of 2 : 1 adducts (I), olefins, and hydroxyarsonium salts[70,112–115]:



Adduct (I) has a structure with a symmetrical hydrogen bond between the oxygen atoms and an ionic or covalent bond between the hydrogen atom and the halogen: $[R_3AsO...H...OAsR_3]^{\oplus}\,Hal^{\ominus}$.[116] Analogous products have also been isolated in the reaction of triphenylarsine oxides with monohalogenoacetate esters, chloroacetone, and chloroacetonitrile[117].

If the arsenic atom is linked to even one aliphatic carbon atom, then, together with the reactions indicated above, the retro-Arbuzov rearrangement of the arsine oxides

(yield from 7 to 75%) takes place, as for arsonic and arsinic esters[118–122]:

$$R_3AsO + R'Hal \rightarrow R_3AsOR' .$$

The mechanism of the reaction of arsine oxides with alkyl halides has been studied in many investigations[19,70,123–127] and, although there are certain discrepancies in the treatment of the individual stages of the reaction by different workers, there is no doubt about the first reaction stage—the nucleophilic attack by the oxygen of the arsenyl group on the α-carbon atom of the alkyl halide, leading to the formation of an alkoxyarsonium salt:

$$R_3AsO + HalCR'_2 - CHR''_2 \rightarrow [R_3AsOCR'_2 - CHR''_2]^{\oplus}Hal^{\ominus}.$$

Further reactions of the alkoxyarsonium salt are also determined by the nature of the reactants and the reaction conditions:

$$[R_3AsOCR'_2 - CHR''_2]^{\oplus}Hal^{\ominus} \rightarrow \begin{cases} \xrightarrow{a} R_3AsOCR'_2 - CHR''_2 + RHal \\ \xrightarrow[b]{+R_3AsO} CR'_2 = CR''_2 + [HOAsR_3]^{\oplus}Hal^{\ominus} \rightarrow 2R_3AsO \cdot HHal . \end{cases}$$

The retro-Arbuzov rearrangement (*a*) takes place when the nucleophile attacks the α-carbon atom of the alkoxyarsonium salt, as for arsonic and arsinic acid esters. Pathway (*b*), involving the abstraction of a proton from the β-carbon atom of the alkoxy-group of the arsonium cation by another arsine oxide molecule, obtains only for arsine oxides. Evidently, as a consequence of the higher basicity of arsine oxides compared with other compounds of tetracoordinate arsenic, they are capable of competing with another nucleophile present in the reaction sphere, namely the halide anion. The large size of the nucleophile (arsine oxide) apparently precludes α-elimination accompanied by the formation of aldehydes (as for arsonic and arsinic acid esters), as a result of which β-elimination, leading to the formation of an olefin, takes place.

In the reaction of trialkylarsine oxides with acid halides, there is a rearrangement analogous to the retro-Arbuzov rearrangement (yield 95%):[120]

$$Pr_3AsO + CH_3COCl \rightarrow Pr_3AsOCCH_3 .$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad O$$

However, the reactions of triphenylarsine oxide with acetyl bromide and chloride result in the formation of dihalogenoarsoranes[128,129]:

$$Ph_3AsO + CH_3COHal_2 \rightarrow Ph_3AsHal_2 + (CH_3CO)_2O .$$

Such substitution also takes place in the reaction of triphenylarsine oxide with phosgene[130]:

$$Ph_3AsY + COCl_2 \rightarrow Ph_3AsCl_2 + COY ;$$
$$Y = O \text{ or } S$$

and with arsenic trichloride[131].

Depending on the structure, arsine oxides react with hydrogen halides in different ways[132–135]:

$$\underset{(I)}{R_3AsO} + HX \rightleftarrows R_3AsO \ldots \underset{(II)}{HX} \rightarrow \underset{(II)}{[R_3AsOH]^{\oplus}X^{\ominus}} \rightleftarrows \underset{(III)}{R_3AsX_2} + H_2O .$$

The reaction of tertiary arsine oxides, having a comparatively low basicity, for example, the derivatives of dihydrophenarsazine, stops at the first stage involving the formation of hydrogen-bonded adducts (with partial proton transfer[134]). Complete proton transfer to the oxygen of the arsenyl group leads to the formation of a salt-like product (II) [113,133,135,136], which can be dehydrated in the presence of an excess of hydrogen halides with formation of dihalogenoarsorane (III).[132,133].

Summarising the entire complex range of reactions occurring when oxygen-containing compounds of tetracoordinate arsenic interact with electrophiles, one can distinguish four principal pathways: the retro-Arbuzov rearrangement (*a*) characteristic of arsenyl compounds having at least one C_{aliph}–As bond; the protonation of the oxygen of the arsenyl group with formation of a hydroxyarsonium salt (*b*), which can undergo further reactions; the exchange reaction (*c*), which can lead not only to the formation of new arsenyl compounds but also to the regeneration of the initial reactants; the reduction of the initial arsenyl compounds (*d*), which usually occurs at elevated temperatures:

$$R_3AsO + R'X \begin{cases} \xrightarrow{a} R_2AsOR' \\ \xrightarrow{b} [R_3AsOH]X \begin{cases} \xrightarrow{+R'X} R_3AsX_2 \\ \xrightarrow{+R_3AsO} 2R_3AsO \cdot HX ; \end{cases} \\ \underset{c}{\rightleftarrows} R_2AsOR' + RX \\ \qquad\qquad\quad \| \\ \qquad\qquad\quad O \\ \xrightarrow{d} R_3As \end{cases}$$

$R = Ar$, Alk or OAlk; $R' = HAlk$, CH_2COR, CH_2CCN, CH_2CCH_3, AlkMg, CCl_3COOH or $AsCl_3$; $X = Hal$.

In all these reactions the primary step is nucleophilic attack by the oxygen of the arsenyl group on the electrophile, leading to the formation of alkoxyarsonium salts.

Thus onion salts play the main role in the reactions of compounds of tetracoordinate arsenic with electrophiles. Analogous onion salts are also formed in the reactions of other oxa-bases R_nEO with electrophiles. In the reactions of phosphoryl compounds with alkyl halides, quasi-phosphonium salts are formed[137]:

$$\underset{\|}{R_2POR'} + R''Hal \rightarrow [R_2P(OR')(OR'')]^{\oplus}Hal^{\ominus} \rightarrow \underset{\|}{R_2POR''} + R'Hal , \qquad (2)$$
$$O \qquad\qquad\qquad\qquad\qquad\qquad O$$

in the reactions of amine oxides the products are alkoxyammonium salts[138]:

$$R'CH_2Hal + R_3NO \rightarrow [R_3NOCH_2R']^{\oplus}Hal^{\ominus} \rightarrow R'C\begin{matrix} O \\ \diagup\!\!\diagdown \\ H \end{matrix} + R_3N , \qquad (3)$$

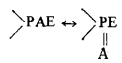
and in the reactions of sulphide oxides the products are alkoxysulphonium salts $[R_2SOR']^{\oplus}Hal^{\ominus}$.[65]

Alkoxyarsonium salts are extremely reactive, so that attempts to obtain them by alkylating arsine oxides did not lead to the desired result at −75 °C even when the halide anion was replaced by the less reactive perchlorate and tetrafluoroborate anions[139]. Instead of alkoxyarsonium salts, the adduct of the arsine oxide with the corresponding acid, $2R_3AsO.HX$, was always isolated.

Alkoxyarsonium salts have been obtained by the reaction of tertiary arsines with t-butyl hypohalites at temperatures in the range between −5° and −10 °C [140,141] and by the reaction of methyl dimethylarsinite with methyl iodide[142]. A whole series of products, usually observed in the pyrolysis of arsine oxides[19], were isolated in the thermal decomposition of alkoxyarsonium salts[140]. In addition t-butyl halide and arsine oxide were isolated, which constitutes indirect evidence for the possibility of an exchange reaction when arsine oxides interact with alkyl halides, giving rise to the regeneration of the arsenyl group (this corresponds to pathway *b* in scheme 1), which indicates that processes of the same type occur in the interaction of compounds of tetracoordinate arsenic (arsine oxides and arsonic and arsinic acid esters) with alkyl halides.

Trimethylmethoxyarsonium iodide interacts instantaneously with arsine oxide, forming the usual adduct $2Me_3AsO.HI$,[142] which confirms the hypothesis[124-126] that the rate-limiting stage of the reaction of arsine oxides with alkyl halides is the formation of alkoxyarsonium salts. The report[143] of the synthesis of an alkoxyarsonium salt from tripropylarsine oxide and ethyl bromide on refluxing the components in benzene is evidently erroneous.

A rearrangement of the type of the retro-Arbuzov rearrangement, which is common for arsenyl compounds, is not characteristic of phosphoryl compounds, for which the bond equilibrium



is displaced towards the tetracoordination form for E = H or C and A = O or S; only for E = P is there a possibility of the existence of both tautomeric forms[144].

The possibility of the retro-Arbuzov rearrangement is determined by the mode of nucleophilic attack on the alkoxyonium cation $[C_{aliph}-E-OC]^{\oplus}$. When E = As, the nucleophile attacks preferentially the α-carbon atom at the arsenic atom, whereas for E = P the attack by the nucleophile is directed to the α-carbon atom of the alkoxy-group. This finding can be explained as follows. Firstly, the strength of the $C_{aliph}-As$ bond is much lower than the strength of the $C_{aliph}-P$ bond in analogous compounds (by 40.2 kJ mol^{-1} and more).[69,145] Secondly the arsonium cation should be stabilised preferentially via an inductive mechanism: $C \rightarrow C \rightarrow As^{\oplus} \leftarrow O \leftarrow C$. The $p_\pi-d_\pi$ interaction of the oxygen and arsenic atoms is then weak or absent, while in the stabilisation of the alkoxyphosphonium cation $p_\pi-d_\pi$ conjugation should play a significant role and should therefore lead to considerable positive polarisation of the α-carbon atom of the alkoxy-group, which facilitates in its turn nucleophilic attack on this atom.

In contrast to the reactions of compounds of tetracoordinate arsenic with electrophiles described above, the reaction of trialkyl arsenates, which have the smallest basicity among arsenyl compounds[71], with electrophiles such as arsenic trihalides and phosphorus trichloride takes place with the retention of the arsenyl group and the formation of tetra-alkyl meta-arsenates[146,147]:

$$2\,(RO)_3AsO + 2AsHal_3 \rightarrow (ROAsO_2)_2 + 2RHal + 2ROAsHal_2\ .$$

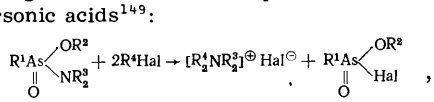
The interaction of trialkyl arsenates with phosphorus trichloride is also complicated by an oxidation-reduction reaction in which trialkyl arsenate behaves as an oxidant:

$$(RO)_3AsO + PCl_3 \rightarrow (RO)_3PO + AsCl_3\ .$$

A similar oxidation-reduction reaction has also been observed in the interaction of arsine oxides and tertiary phosphines[148]:

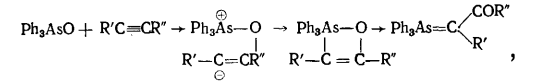
$$R_3AsO + R_3P \rightarrow R_3PO + R_3As\ .$$

In the reactions of amidoesters of arsonic acids with electrophiles (alkyl halides and halogenoesters) a competition might have been expected between the two nucleophilic centres of the amidoester molecule—the oxygen atom of the arsenyl group and the nitrogen atom of the amido-group. However, the study of the products of these reactions showed that the nitrogen atom is the nucleophilic centre in the amidoesters of arsonic acids[149]:



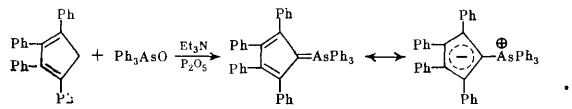
which also agrees with the conclusion that these derivatives are protonated at the nitrogen atom[71,80].

The nucleophilic reactivity of arsenyl compounds in relation to an unsaturated carbon atom is manifested, for example, in the reactions of triphenylarsine oxide with highly electrophilic reagents such as activated acetylenes (dicyanoacetylene and others).[148] It has been suggested that the reaction proceeds via the formation of a zwitterion:

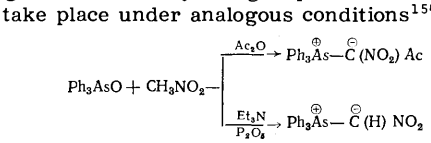


and that the ylid formed as a result of the reaction is resonance-stabilised. Triphenylphosphine oxide is less reactive in this kind of reaction because it reacts only with dicyanoacetylene and at a higher temperature than triphenylarsine oxide[148].

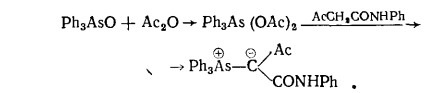
The condensation of triphenylarsine oxide with substituted cyclopentadienes, which takes place in acetic anhydride[150,151] or in triethylamine in the presence of phosphorus pentoxide[152,153], also leads to ylids:



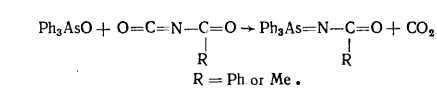
The reactions of tertiary arsine oxides with compounds containing activated methylene groups and also with nitromethane take place under analogous conditions[154]:



The role of acetic anhydride in these reactions reduces to the formation of the intermediate diacetoxyarsorane[153-155], which can subsequently react with compounds containing activated methylene groups, giving rise to the corresponding ylids[155]:

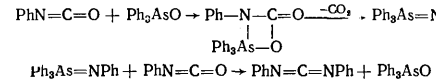


The reactions of stabilised isocyanates with triphenylarsine oxide also lead to the formation of arsine imides[156]:



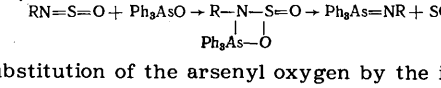
The benzoyl- and acetyl-arsine imides formed under these conditions are also resonance-stabilised.

The interaction of triphenylarsine oxide with phenyl isocyanate leads to the formation of diphenylcarbodi-imide[157]:

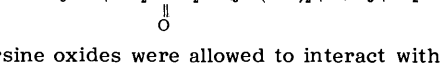


However, under mild conditions the reaction stops at the first stage, involving the formation of arsine imide[158].

N-Sulphinamides react analogously with triphenylarsine oxide[58,159]:



The substitution of the arsenyl oxygen by the isocyanate group takes place in the reactions of tertiary arsine oxides with urea[160,161]:



When arsine oxides were allowed to interact with diols in

benzene with azeotropic distillation of the water formed, cyclic esters of pentacoordinate arsenic—dioxa-arsolanes—were obtained[162]:

$$R_3AsO + \begin{matrix} HO \\ HO \end{matrix} \xrightarrow{-H_2O} R_3As\begin{matrix} O \\ O \end{matrix}$$

Under analogous conditions, phosphine oxides do not form the corresponding dioxaphospholanes. The interaction of stibine oxides with diols also results in the formation of dioxastibolanes[163].

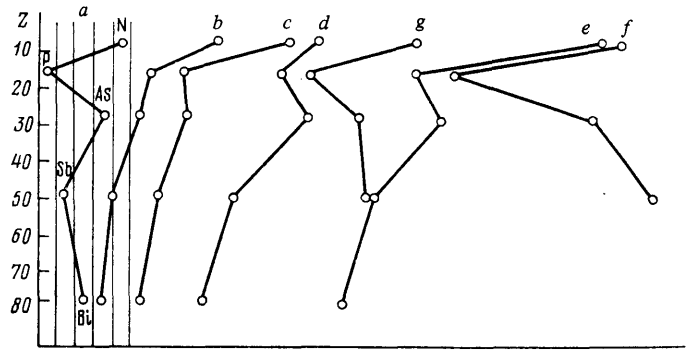
Nucleophilic addition to the carbonyl group is a general reaction for carbonyl-containing compounds; in particular, ketones interact with α-glycols to form quantitatively the corresponding cyclic ketals[164]. By analogy with carbonyl compounds, for which the mechanism of reactions involving nucleophilic addition to the carbonyl group has been studied in detail[165,166], it has been suggested that the mechanism of the reactions of arsine oxides with diols is based on proton transfer from the diols to the oxygen of the arsenyl group with formation of a new arsenic–oxygen bond and subsequent dehydration of the intermediate formed[162].

V. THE PROBLEM OF ANALOGY IN GROUP VA OF THE PERIODIC SYSTEM

Examination of certain physicochemical and chemical properties of arsenyl compounds and their comparison with those of the oxa-bases R_3EO, where E is a Group VA element makes it possible to put forward certain considerations concerning the problem of analogy in Group VA. This problem is closely related to the more general problem of the analogy of the elements within any Group. Examination of the properties of organoelemental compounds on the basis of the properties of the elements and hence of their positions in the Periodic System is extremely important, because it provides a guideline which enables one to become orientated in the enormously wide variety of organoelemental compounds and their properties. It has been mentioned in a number of studies[167–170] that the simplified formulation of the Periodic System, widely used at the present time, in which the elements of the main subgroups are arranged in vertical columns, had led to some 'fetishisation' of the properties of these elements and to the widespread delusion that there is a gradual and smooth increase of the changes in the properties of the elements and their compounds.

Without attempting to consider the historical aspects of the development of various formulations of the Periodic System, we shall confine ourselves to mentioning studies in which the problem of analogy in Group VA was directly involved. Evidently one should mention that in the form of the Periodic System proposed by Mendeleev the elements of the Second Period are displaced relative to the heavier elements, which emphasises their special role. In the pyramidal form of the Periodic System proposed by Nekrasov[171] the elements of the Second and Third Periods are isolated. From the standpoint of Nekrasov's ideas concerning complete and incomplete electronic analogues, nitrogen and phosphorus and also arsenic, antimony, and bismuth are complete electronic analogues, while phosphorus and arsenic are incomplete analogues. This modification of the Periodic System takes into account the electronic structures not only of neutral atoms but also of all the characteristic valence states of the elements.

Subsequent studies in which the problems of the analogy of the elements of the Periodic System were developed and new forms of the Periodic System were proposed, reflecting finer differences between analogous elements, were based on the allowance for the structural and energetic characteristics not only of the outer electron shells of atoms but also of the two electron shells immediately preceeding the outer shell[167–170]. On the basis of the analysis of the energetic characteristics of the atoms (ionisation potentials, electron affinities, orbital radii, etc.), Godovikov[169,170] proposed an improved form of the Periodic System. Two variants of the subdivision of the elements into small subgroups were proposed for Group VA: first variant: VA1(N), VA2(P, As, Sb), VA3(Bi); it agrees well with the analysis of the properties of the oxygen compounds of the elements; second variant: VA1(N), VA2(P), VA3(As, Sb), VA4(Bi); it agrees with the properties of the sulphides.



Dependence of certain parameters of Group VA elements and their compounds on the atomic number Z of the element in the Periodic System: *a*) the arrangement of analogous Group VA elements in the matrix form of the Periodic System[167]; *b*) the first ionisation potentials of the elements[169]; *c*) the change Δr(Å) in the difference between the orbital radius of the atom and the radius of its occupied electron shell immediately preceding the outer shell in analogous elements[169]; *d*) electron affinity[69]; *e*) electronegativity[172]; *f*) pK_a for R_3EO;[89] *g*) E=O bond energy in R_3EO.[58,69].

A similar approach to the construction of the Periodic System with displacements was used by Grigorovich[167,168], who proposed a matrix form of the Periodic System, which provides for the subdivision of the main subgroups of Groups II–VII into five items (see Figure, *a*). This subdivision is based on the variation of the structures of the inner electron shells and the variation of the binding of the outer electrons to the nucleus. Although the matrix form of the Periodic System has not received its due recognition among chemists, nevertheless it reflects most clearly the non-monotonic, frequently zigzag, variation of the physical properties of the elements of the subgroup. This finding is also emphasised in Godovikov's studies[169,170]. The Figure presents plots of the variation of certain properties of Group VA elements and their compounds, illustrating the above postulate. The non-monotonic variation within a subgroup of fundamental properties of the elements such as electronegativities, ionisation potentials, electron affinities, orbital radii, etc., leads to a non-monotonic, frequently zigzag, variation of the physicochemical properties of organoelemental compounds (such as the E=O bond energy and pK_a). This type of variation of the physical and

physicochemical parameters of organoelemental compounds should evidently affect also the variation of their chemical properties.

Analysis of the arrangement of analogous elements within a subgroup, proposed in the matrix form of the Periodic System, explains the similarity of many physicochemical and chemical properties of nitrogen and arsenic compounds which are more likely to be regarded as an anomaly when the usual Periodic System is employed. The similarity of the physicochemical characteristics of the AsO and NO groups as well as of the electron-donating capacities of the oxa-bases R_3NO and R_3AsO was mentioned above. Such similarity has also been observed on comparing the chemical behaviour of the oxa-bases of nitrogen and arsenic, for example, their capacities for the tautomeric transformation

$$R_3EO \rightarrow R_2EOR,$$
$$E = N \text{ or } As.$$

In the N, P, As triad in the matrix form of the Periodic System the phosphorus atom is displaced to the extreme left-hand position (*a*) due to the strong shielding effect of the s^2p^6 electrons, which is greater than that of the $s^2p^6d^{10}$ electrons of arsenic and s^2 electrons of nitrogen. This is evidently also responsible for the specificity of the properties of many phosphorus compounds. The arsenic atom in the matrix form of the Periodic System occupies an intermediate position with some displacement towards nitrogen (see Figure, *a*). This intermediate position of arsenic is reflected in the reactions of the compounds R_3EO with alkyl halides. Comparison of arsenyl compounds in these reactions [scheme (1)] with phosphoryl compounds [scheme (2)] and amine oxides [scheme (3)] shows that arsenyl compounds undergo transformations which are characteristic also of amine oxides—an oxidation-reduction reaction [scheme (1), pathway *a*]—and of phosphoryl compounds—an exchange reaction [scheme (1), pathway *b*].

In the search for similarity, one must not forget the uniqueness of each element of the subgroup. The advantage of the matrix form of the Periodic System also consists in the fact that it reflects not only the similarities but also the differences between the properties of analogous elements caused by the differences between the structures of their inner shells, while the structures of the outer shells are similar.

The problem of the analogy of the elements and their compounds is one of the exciting problems in chemistry. The present review is in essence limited solely to the indication of the new possibilities of the analysis of this problem, which have arisen in connection with the development of new improved formulations of the Periodic System.

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The Regularity Bands in the Infrared Spectra of Polymers with Distortions in Structural Periodicity

I.V.Kumpanenko and N.V.Chukanov

Studies of the microstructures of polymers by methods based on the measurement of infrared band intensities are examined. The cluster model, within the framework of which a band classification has been proposed and the possibilities of infrared spectroscopy for the determination of different structural parameters of macromolecules have been analysed, is justified. The bibliography includes 142 references.

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I. INTRODUCTION

The latest advances in both practical and theoretical infrared spectroscopy of polymers are associated primarily with the study of the structures and vibrational properties of macromolecules with more or less pronounced distortions in structural periodicity. The interest in these studies is understandable because the vast majority of polymeric materials consist precisely of such macromolecules and the microstructures of polymer chains are known to influence directly or indirectly the physicochemical properties of polymers and to reflect the mechanisms of their formation.

Much attention is devoted in these studies to the analysis of the maximum intensities of the so-called regularity bands; this is mainly because, among all the spectural parameters, this one is perhaps the most sensitive to the degree of order in the macromolecular structure. In the course of its development the modern vibrational spectroscopy of polymers has encountered many problems and it appears useful to begin the review with their brief examination.

II. FUNDAMENTAL PROBLEMS OF THE INFRARED SPECTROSCOPY OF IRREGULAR POLYMERS

For many years infrared spectroscopy remained and still remains one of the most accessible and universal instruments for the investigation of the microstructures of polymers, and empirical methods of interpreting the experimental results still occupy a notable position in it. By varying any structural parameters, for example the length of the entire macromolecule or of its regular component, the degree of tacticity, or the sequence length of the polymer, the investigator is able to discover the spectral changes arising under these conditions, which are then used in the form of calibration relations in the study of the structures of a wider range of compounds.

In the last two decades there has been a growth of interest in the vibratonal spectroscopy of irregular polymers also among theoreticians. A series of new approaches have been created on the basis of the perturbation theory[1,2] and numerical methods[3-5] and attempts have been made to apply the methods of the dynamic theory of defective crystals, which have been well known for a long time in solid state physics, such as the method of Green functions[6-9], the method of negative eigenvalues[10,11], the method of transport matrices[12,13], and the method of moments[14] for the analysis of the vibrational spectra of real macromolecules. There are in general no fundamental obstacles to their application, but there are certain difficulties associated with the large number of vibrational degrees of freedom in the repeating monomeric unit, and, what is more significant from the standpoint of practical applications, with the wide variety of types of distortions in the regularity of the structure within the limits of a single chain.

Procedures widely known in theoretical spectroscopy are used to overcome the first difficulty. For example, in the so-called skeletal approximation[6,7,15,16] some of the atomic groups are replaced by point masses. In the method of bound oscillators[1,17] the repeating monomeric unit is modelled by oscillating dipoles, whose frequencies correspond approximately to the "normal" frequencies of the isolated units. There exist also other approaches[1,2] but we shall not consider them.

In the analysis — both theoretical and experimental — of the spectroscopic manifestations of structural distortions it is possible to proceed via two pathways. The first pathway involves a scrupulous allowance for all the versions of the structure by observing and analysing the spectral lines reflecting the vibrations of the corresponding molecular fragments. The experimental studies based on this approach began to appear literally from the instant of the introduction of infrared spectroscopy into practical laboratory research and nowadays they still make a very considerable contribution. Serious theoretical studies have recently begun to appear in this field. Among these, we may mention as an example studies[10,18] in which determinations were made by the method of negative eigenvalues of the frequency distribution in the spectra of hydrocarbons with different combinations of conformers, both specified artificially and generated at random, or studies[1,19-22] in which calculations were made by the authors' novel method[23-26] of the frequencies and intensities of the infrared bands in the spectra of a series of polymers with different configurational and conformational variants of the chain structure.

The second pathway is associated with the study of the behaviour of the infrared bands reflecting the vibrations of structurally regular frequencies of monomeric units in polymer chains; the nature of the defects terminating these sequencies is then usually not specified and it is implied that

their concentration is fairly small. This pathway is extremely promising, as can be seen from the rapid increase of the number of publications, in which, however, the validity of the application of this approach is usually not analysed.

The differentiation of research trends mentioned above is based on the existence of two types of spectral bands, namely bands due to local vibratons, i.e. vibrations localised in the vicinity of defective units or fragments whose intensity and frequency depend mainly on the nature and concentration of these defects, and bands due to chain vibrations in which the large regular sections of the chain distributed between the defects vibrate as a single whole and whose spectroscopic parameters depend only slightly, in contrast to the previous bands, on the nature of the defects, being determined mainly by the structure and length of the periodic part of the chain.

The sub-division of vibrations into local and chain vibrations is arbitrary: in a vibrating system there is always a greater or smaller mixing of such vibrations but in many instances such mixing is nevertheless insignificant and may be treated as a perturbation and taken into account appropriately. In a more rigorous approach it is also necessary to take into account the possibility of the appearance of quasi-local or resonance vibrations[27,28], the use of which for the analysis of the structure in the sense indicated is incorrect.

The polymer chain can naturally be so disordered that there can be no question of the existence of any chain vibrations embracing large sections of macromolecules. However, many problems of practical importance are associated precisely with the analysis of the microstructures of polymers with molecules containing fairly long regular segments interrupted by individual defective units or small irregular fragments.

The approximation, in which account is taken only of the vibrations of the regular chain sections and the mutual independence of the vibrations of different regular sections within the limits of the same chain is postulated, is referred to as the cluster approximation and plays a very important role in spectroscopic studies. In the majority of investigations by vibrational spectroscopic methods of the stereoregularity of polymers[29-31], the conformations of macromolecules in solution[32-34], the sequence length of copolymers[35-48], and the degree of branching of polymers[49], the cluster approximation is in essence employed, although this is frequently not stipulated. In view of the particular importance of this approximation for the subsequent description, Section III of this review is devoted to a brief analysis of its principles.

The chain vibration bands satisfying the criteria of the cluster approximation are of special interest in our case, since they include the regularity bands according to Zerbi's classification[50]. In a series of studies[29-31,35-48] bands of this type have been referred to as spirality, iso- or syndiotacticity, etc., bands. It is noteworthy that such terms are not entirely unambiguous. For example, the isotacticity band at 998 cm^{-1} in the spectrum of polypropylene can be referred to simultaneously also as the helix band, since the changes it undergoes with decrease of the length of the macromolecular helix observed on fusion of the polymer are broadly the same as those occurring following a decrease of the degree of its isotacticity[30].

In many instances the frequency of the maximum of such a band is independent of or depends only slightly on the regularity of the macromolecule and the band intensity is the structure-sensitive parameter. Henceforth, in speaking of regularity bands, we shall have in mind precisely such bands.

A number of characteristics of the behaviour of regularity bands can be discovered by following the changes in them when the structure of the macrochains is varied. As a rule, these bands appear in the spectra when the regular, in both structural and chemical respects, sequence of monomeric units reaches a critical length, characteristic of precisely this band. For example, the 973 and 998 cm^{-1} bands in the spectra of ethylene–propylene copolymers arise when the isotactic polypropylene sequences reach lengths of 5 and 10 units respectively[35,36], while the 565 and 750 cm^{-1} bands in the spectra of epoxypropane–tetrahydrofuran copolymers refer to the vibrations of polytetrahydrofuran fragments containing at least 4 and 2 units respectively[47].

Another important feature of the regularity bands is the monotonic increase of their intensity with increase of the average length $\bar{N}$ of the regular sequences of units in the polymer and the more or less rapid attainment of a limiting intensity for fairly high values of $\bar{N}$. The increase of the maximum intensity can take place both owing to the increase of the integral band intensity and owing to the decrease of the half-width of the band.

The very fact that the band intensity depends on the length of the regular segments in polymer chains usually leads to the possibility of using this relation to analyse polymer microstructures, in particular, the possibility of measuring the average sequence length of the copolymers and of the degree of tacticity of stereoregular homopolymers. However, the problem of whether such measurements are sufficiently correct and of the nature of the averaging in the experimental determination of these quantities have still not been adequately investigated.

This review is devoted to a detailed analysis of the factors influencing the dependence of the chain vibration band intensities and widths in the infared spectra of polymers on the lengths of structurally regular sequences of units. The criteria governing the choice of regularity bands, both with the aid of a set of empirical features and on the basis of an *a priori* investigation of the structural-force characteristics of macrochains are analysed. Some attention has been devoted to bands containing information about the structure of the helix and to crystallinity bands.

III. THE STRUCTURAL MODEL AND THE CLUSTER APPROXIMATION

A configurationally regular polymer chain is known[51] to be capable of passing under certain conditions to a conformationally regular state. This transition is accompanied by the occurrence of the so-called long-range conformational order in which the chain consists of an ideal helix with the corresponding spatial symmetry. The formation of fairly long helical fragments can be observed in the crystallisation of a polymer or (sometimes) with decrease of the temperature of its solutions.

We shall now assume that under the experimental conditions all the configurationally regular fragments of the macromolecules have passed to the conformationally regular helical state. In this case the fraction of conformationally regular segments attain saturation due solely to the configurational or chemical defects and the distribution of the helices in the specimen with respect to length reflects and to the length distribution of the regular sequences of the monomeric units in the polymer. The necessity for monitoring the conformational defectiveness in the course of spectroscopic measurements becomes clear from the foregoing, since its presence can lead to an apparent decrease of the degree of configurational irregularity of the polymer determined from spectroscopic data.

The main idea of the cluster approximation consists in the fact that, in the analysis of vibrations, the polymer molecule, consisting of alternating regular helical sections and defective regions, is imagined to be ruptured at the sites of the defects and the vibrational spectrum of such a molecule in the frequency range of the chain vibration analysed is represented as a superposition of the vibrational spectra of mutually independent helices.

We emphasise that not all spectral regions satisfy the cluster approximation. The existence of local vibrations of the defects, the occurrence of quasi-local or resonance vibrations—all these can hinder or preclude the application of a given frequency range to structural analysis in terms of the given approximation. A test of the applicability of the cluster approximation in each specific instance can be carried out either experimentally by analysing the spectra of model compounds or theoretically.

The experimental test can consist, for example, in comparing the spectra of polymer specimens differing in the nature of the defects. The application of the cluster approximation is correct for bands whose frequency and intensity vary little in a series of polymers having identical distributions of regular segments with respect to length but containing defects of different types.

In the majority of experimental studies where the cluster approximation has in fact been used for the analysis of polymer microstructures (albeit without the term itself being actually employed), such a test has been carried out in one way or another. Fig.1 illustrates the results of one of the versions of such an investigation for the low-frequency 720 cm^{-1} band for a system of wagging-torsional vibrations of polymethylene fragments in polymer chains of different structure. Evidently the dependence of the relative intensities on the lengths of the regular polymethylene segments in a series of specimens with different types of distortions in structural regularity fits on a single curve, which constitutes an experimental confirmation of the possibility of employing the cluster approximation in the given instance[142].

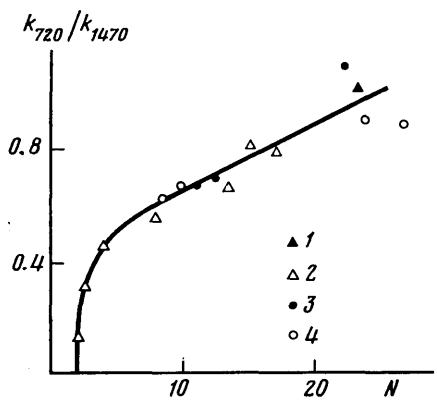


Figure 1. Dependence of the absorption coefficient of the wagging vibration band (720 cm^{-1}), referred to the absorption coefficient of the scissors vibration band (1470 cm^{-1}), on the average length of the polymethylene segments for n-paraffins(1) and copolymers of ethylene with ethylene-d_4(2), but-1-ene(3), and allene(4) at room temperature[142].

Another experimental test is based on the analysis of the form of the dependence of the band intensities on the lengths of regular segments; this will be discussed in detail in Section VI.

The question of the theoretical criteria of the applicability of the cluster approximation has been studied in detail[52] and we shall consider briefly the final results of these studies. The introduction of a defective unit into an initially ideal polymer chain leads in general to complex changes in the vibrational spectrum of the macrochain as a whole. With some approximation, these changes reduce to the appearance of local and resonance vibrations and the mixing of various chain vibrations. At the same time it can be shown that, when certain relations between structural-force parameters of the regular part of the chain and of the defective units are fulfilled, one or several of the chain vibrations of the fragment, located between two defects, can be regarded as independent of all other chain vibrations; it is then immaterial whether the latter refer to the given fragment, to defective units, or to adjacent sections of the chain.

Anticipating, we emphasise that the structure and parameters of the force fields of the majority of real polymeric molecules are such that a fairly large number of bands, referring to this type of independent chain vibrations of regular fragments or, in other words, bands satisfying the criteria of the cluster approximation, can always be found in their vibrational spectra.

These criteria assume the simplest form in terms of the so-called normal coordinates of the repeating unit (NCRU). In terms of these coordinates, the vibrating polymer chain with r degrees of freedom in a repeating unit can be represented by a set of r systems of linked oscillators and each of its r frequency branches forms its own system, which in the case of a defect-free chain is independent of the remaining systems. These coordinates can be referred to as the natural coordinates of the model of linked oscillators. A transformation whereby one can achieve a conversion to such coordinates from any initial coordinates, for example, from cartesian or natural coordinates, has been proposed[53].

The application of this transformation makes it possible to calculate the parameters of systems of linked oscillators modelling any polymer molecule including, among others, an irregular molecule, from its force constants specified in terms of any representation, for example, in the generalised valence force field representation.

The possibility of determining the parameters of the model of linked oscillators in the vicinity of "defective units" of the polymer chain appears to be the most important in this instance. These parameters can then be readily tested for their correspondence to the criteria of the cluster approximation.

Readers interested in further details of this problem are referred to Chukanov and coworkers[52,53]. Here we shall attempt to illustrate the theoretical criteria of the applicability of the cluster approximation in relation to the example of a hypothetical regular polymer molecule with a single defect and two degrees of freedom in the repeating unit. Such a molecule can be brought into correspondence with the model of linked oscillators illustrated schematically in Fig.2. In this model oscillators with intrinsic frequencies ω and ω' are combined into two chains via elastic forces with bond constants α and α'. The interaction between the chains with a force constant δ takes place only via "defective" oscillators, whose frequencies are ω_e and ω_e' and whose linkage to the periodic component of the chains is described by the interaction constants β and β' respectively. The fulfillment of the

conditions

$$\begin{aligned} |\beta| &\ll |\omega^2 - \omega_e^2| \\ |\delta| &\ll |\omega_e^2 - (\omega_e')^2| \\ |\beta'| &\ll |(\omega')^2 - (\omega_e')^2| \end{aligned} \qquad (1)$$

leads to the "breakdown" of such an integral vibrational system into four oscillator chains, each of which vibrates independently of the others[52].

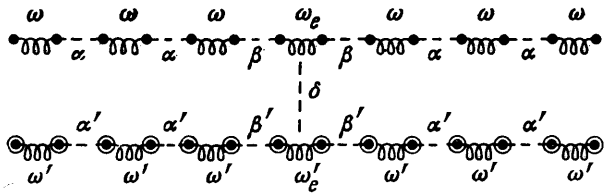


Figure 2. The system of linked oscillators modelling a polymer molecule with two degrees of freedom in the repeating cell and a single defective unit.

We may note that the fulfillment of only the first or only the last relation (1) makes it possible to apply the cluster approximation to oscillator chains with frequencies ω and ω' respectively.

Eqns.(1) thus express the quantitative criteria of the applicability of the cluster approximation to the system considered. In a more general approach one must naturally compare the vibrational frequency of a defective oscillator with the frequency of the chain vibration under consideration and not with the frequency of the intrinsic vibration of an individual non-defective oscillator.

The treatment in all subsequent sections of this review is based on the cluster approximation. Here it is understood that all the spectral bands analysed satisfy the theoretical or experimental criteria of this approximation.

IV. AN EMPIRICAL APPROACH TO THE STUDY OF THE MICROSTRUCTURES OF POLYMERS

Numerous experimental data which have accumulated hitherto indicate the possibility of deriving specific relations for the entire wide variety of spectroscopic manifestations accompanying the structural changes in polymers. Analysis of relations of this kind is very greatly simplified by employing the cluster approximation. Above, it was already noted that the cluster approximation has in fact been used for a long time in experimental studies of polymer spectra. In this section we shall consider studies of this kind, which will be grouped in terms of the types of bands whose intensity is sensitive to particular characteristics of the polymer structure.

Among all the infrared bands, it is reasonable to isolate three large groups from the standpoint of the study of the microstructure: the bands due to the local vibrations of the defects, the characteristic bands of the repeating units, and the regularity bands.

1. The Bands of the Local Vibrations of Defects

The criteria of the cluster approximation (1) at the same time constitute the criteria of the local nature of the vibrations of the defective unit to which correspond oscillators with frequencies ω_e and ω_e' in the NCRU system. However, in practice the demonstration of the local nature of the vibrations does not necessitate the use of Eqns.(1) in each case; it is sufficient to show merely that in a series of polymers with different degrees of regularity the frequency of the given vibration is constant and the intensity of the corresponding band is proportional to the concentration of defects of the given type.

This simplest type of vibration can in fact be used to investigate a whole series of structural characteristics. These include, firstly, the analysis of *the nature and concentration of the terminal functional groups*. The relevant methods have been developed for poly(ethylene terephthalate)[54], poly(ethylene glycol)[34,55], polystyrene (carbonyl groups)[56], and other polymers[34]. In a number of studies the local vibration bands have been used to determine the degree of branching of polyethylene[57,58], poly(vinyl chloride)[59], polycaproamide[60], ethylene-vinyl acetate copolymers[61], and others[34].

The knowledge of the concentration of the functional groups and also of the degree of branching makes it possible to estimate the *functionality* of the oligomer, which is important from the standpoint of its subsequent polymerisation. For a polymer with a known functionality, the concentration of the end groups is unambiguously related to *the molecular weight*. The intensities of the local vibrations of the "contacts" between units of different kinds in the copolymer have been used to determine *the average length of the block* in vinyl chloride–vinylidene chloride[41], epoxyethane–epoxypropane[62], and tetrafluorethylene–chlorotrifluoroethylene[63] copolymers.

It has been shown[27] that single distortions of the *stereoregularity* of isotactic polypropylene lead to the development of local vibrations. The concentration of single polyethylene units in ethylene–propene copolymers has been determined[64] from the intensity of the 733 cm^{-1} band.

2. Characteristic Vibrations of the Repeating Chain Units.

The vibrations of the macrochains for which the frequencies and absorption coefficients of the corresponding bands depend only slightly on the regularity of the polymer structure can be assigned to this class. The intensities of these bands are determined mainly by the content in the polymer of units of the given type and can be used, for example, for the analysis of the composition of the copolymer[65].

The bands can apparently be made more characteristic by measuring the spectra of conformationally irregular copolymers; for example, it is possible to investigate copolymers in the form of solutions at high temperatures or melts.

Calibration curves for the determination of the compositions of ethylene–propene[66], ethylene–but-1-ene[67], propene–but-1-ene and propene–oct-1-ene[68], vinyl acetate–vinyl chloride[69], propene–vinyl chloride[70], ethylene–propene and ethylene–hexene[71], ethylene–vinyl acetate[61], epoxyethane–epoxypropane[55], and many other copolymers have been published. The corresponding references can be found in a monograph[34]. Unfortunately the absence of a dependence of the extinction coefficient on the regularity of the polymer has not been tested in all the investigations.

A number of studies in the same series have been devoted to the *isomeric composition* of the polymers, particularly polybutadiene[72], polypentenamer, and polyoctenamer[73].

3. Regularity Bands

As already mentioned, a characteristic feature of bands of this type is a sharp decrease of their intensity (frequently to zero) in those cases where the average length $\bar{N}$ of the regular sequence of monomeric units falls below a certain threshold value N_0.

The factors determining the average length $\bar{N}$ of a regular sequence of units of a given type may be stereoregularity, conformational order, the extent of the block structure (in the copolymer), the molecular weight, and the degree of crystallinity. Depending on the objects of study, the regularity bands can be divided into several types. According to the classification adopted by Zerbi et al.[50], the conformational bands are those whose frequency and intensity depend on the conformational state of the unit. No account is then taken of the fact that the band parameters depend on the conformational state of the neighbouring units, as suggested, for example, by the complete disappearance of certain conformational bands on fusion of the polymers or when the temperature of their solutions is raised[34,37,75]. The latter implies that a threshold length of the regular sequence exists for such conformational bands, as for regularity bands.

Assuming that the absorption coefficient is independent of the length of the conformationally regular sequence, *the conformational structures* of polyethylene[76], poly(ethylene terephthalate)[77], *trans*-1,4-polybutadiene[78], and a number of other polymers have been analysed. In particular, measurements of the spectra of atactic polystyrene in polarised light[79] made it possible to isolate the spectral contribution of fragments having the *trans*-conformation. However, the hypothesis used in the above study[79] that the vibrations are characteristic requires a rigorous proof and by no means always holds. Thus the spectrum of polystyrene contains a band at 540 cm^{-1}, which is sensitive to sequences containing at least four *trans*-C–C bonds in the main chain[40].

The crystallinity bands have been used to determine *the crystal structures* and *degrees of crystallinity* of polyethylene[80–83], polyesters of the type $[-CO-O-(CH_2)_m-]_n$,[84] polybutadiene[85], isotactic poly(vinyl alcohol)[86], poly(vinyl chloride)[87], poly(vinyl-β,β-d_2 chloride)[88], polytetrafluoroethylene[89], and dextran[90], using simultaneously diffuse bands, assigned to the vibrations of the amorphous regions, in some of the studies[80,82,88,90].

The amorphous structure bands occupy a special place among the structure-sensitive bands. Factors such as the presence of "amorphous" conformations, the infringement of selection rules associated with the helical symmetry of the chain, the scatter of the regular helices with respect to length, and fluctuations of the molecular environment play a role in their formation. Since the amorphous structure bands are not regularity bands in the sense defined above, we shall not consider their analysis.

A method has been proposed[91], for the resolution of the spectrum into components referring to the amorphous and crystalline regions on the assumption that their contributions to the spectrum are additive. Having applied this method to the poly(ethylene terephthalate) spectrum, the authors[91] concluded that, although the *trans*--isomers are present in both phases, their characteristic bands, referring to the amorphous phase, are not manifested in the spectrum, since they are smeared out as a consequence of the marked scatter of the intermolecular interaction energies. However, another explanation of this effect is possible, namely one based on the assumption that the lengths of the sequence of *trans*-isomers in the amorphous phase do not reach the threshold lengths for the regularity bands.

Empirical methods for the analysis of the microtacticity of polypropylene have been developed[30,35]. It has been shown that the 998 and 973 cm^{-1} bands appear in the spectrum for lengths of the isotactic chains greater than those corresponding to 10 and 5 units respectively.

A detailed analysis of bands sensitive to isotactic, syndiotactic, and heterotactic sequences in the polyproylene molecule has been carried out[92]. The 690 cm^{-1} band in the poly(vinyl chloride) spectrum is sensitive to the concentration of the isotactic diads[93]. A method for the determination of the concentration of the diads of polybutadiene units in the 1,4-*cis*- and 1,4-*trans*-configurations has been described[94].

The determination of the sequence length of copolymers constitutes an important problem. In most studies devoted to the determination of this parameter with the aid of regularity bands, the power function method was used, according to which the dependence of the absorption coefficient on the length of the regular segment is described by a function of the type

$$k(N) = \begin{cases} 0 \text{ when } N < N_p \\ k \text{ when } N \geqslant N_p \end{cases}$$

The power function method has been used in the analysis of the sequence length of styrene–methyl methacrylate[38], styrene–butadiene and styrene–acrylonitrile[39,95], methyl methacrylate–acrylonitrile[46], ethylene–propene[30,35,96], propene–propene-1,1,2-d_3, styrene–α-monodeuterostyrene[37], tetrahydrofuran–epoxypropane[47], and epoxyethane–epoxypropane[48] copolymers. It is of interest to note that in almost all cases the threshold length of the sequence of monomeric units analysed is almost independent of the nature of the neighbouring blocks. For example, for all the styrene copolymers enumerated above, $N_p = 3–4$ corresponds to the 543 cm^{-1} band, $N_p = 9–11$ corresponds to the 998 cm^{-1} band of isotactic polypropylene fragments, etc. Furthermore, the intensities of the regularity bands in the spectra of the oligomeric fractions and tetrahydrofuran (THF) copolymers depend on N in the same manner[47]. All this demonstrates the applicability of the cluster approximation to the systems enumerated above.

Table 1 presents the results of studies of the regularity bands–their frequencies and the characteristic lengths of the monomeric unit sequences measured with their aid. The quantity N_0 represents the extrapolated average length of the regular segment for which the given band appears in the spectrum and N_p is the length for which the band intensity reaches half its maximum value. Tables 2 and 3 present the analogous lists for crystallinity and amorphous structure bands.

Despite the fact that the intensities of the regularity bands are extremely sensitive to the polymer microstructure, their use for the analysis of sequence length, stereoregularity, etc. is coupled with certain difficulties.

One of the main difficulties is the absence of model compounds necessary for the derivation of calibration relations between the extraction coefficients and the length of the regular chain. The description of these relations with the aid of a power function[37,47] constitutes a fairly rough approximation.

The need to derive a theoretical expression for the function $k(N)$, which must be fairly general and must contain as few as possible empirically determined parameters, follows from the foregoing. The knowledge of this function would

make it possible to solve yet another problem, namely to establish the type of averaging of the lengths of the regular segments in polymers measured with its aid as well as the place of the average quantities in the series of those generally accepted, namely number-average, weight-average, etc. A detailed examination of these problems is presented below.

Table 1. Regularity bands.

Type of regular sequence	ν, cm^{-1}	N_n	N_p	Polymer system	Refs.
Polymethylene	730	11	17	Crystalline orthorhombic n-paraffins	[43]
ditto	720	11	17	ditto	[43]
Isotactic polypropylene	998	—	12	Propene–ethylene copolymers	[30,35,36]
ditto	973	—	4	ditto	[30,35,36]
"	998	—	10	Propene–propene-1,1,2-d_3 copolymers	[37]
"	842	—	10	ditto	[37]
"	899	—	—	Crystalline and amorphous polypropylene	[97]
"	809	—	—	ditto	[97]
cis-1,4-Polybutadiene	778	2	—	Solution of polybutadiene in carbon disulphide	[94]
Isotactic polystyrene	1194	1.5	6	Highly crystalline isotactic styrene–styrene-α-d_1 copolymers	[37]
ditto	1053	2.1	10	ditto	[37]
"	920	—	10	"	[37]
"	1084	—	5	Solutions of isotactic styrene–styrene-α-d_1 copolymers in carbon disulphide at −104 °C	[37]
"	920	—	10	ditto	[37]
"	898	—	16	"	[37]
"	1194	1.8	4	"	[37]
"	543	—	3	Styrene–methyl methacrylate copolymers	[38]
"	540—545	—	4—5	Styrene–butadiene and styrene–acrylonitrile copolymers. Homopolymers	[39,40]
Isotactic poly(vinyl chloride)	1434	—	2	Vinyl chloride–vinylidene chloride copolymers	[41]
ditto	1247	—	3	ditto	[42,44]
Poly(ethylene oxide)	1350	2	5	Solutions of glymes and poly(ethylene glycol) at −90 °C	[43,55]
ditto	1283	2.1	5	ditto	[43,55]
"	1283	0.5	6	Solid glymes, poly(ethylene glycols) and epoxyethane–epoxypropane copolymers	[43]
Polytetrahydrofuran	750	1.1	4	Solutions of oligomers and tetrahydrofuran–epoxypropane copolymers in carbon disulphide at low temperatures	[47]
ditto	565	3.2	6	ditto	[47]
Poly(methyl methacrylate)	1060	—	3	Methyl methacrylate–acrylonitrile copolymers	[46]
Polymethacrylonitrile	1215	—	—	Methacrylonitrile–acrylonitrile copolymers	[45]
Polyacrylonitrile	775	—	—	Homopolymers	[98]

V. DEPENDENCE OF THE INTENSITIES AND WIDTHS OF THE REGULARITY BANDS ON THE LENGTH OF THE MACROMOLECULAR HELIX

In interpreting spectroscopic data, experimenters usually prefer to deal with the absorption coefficients of bands at their maxima (k_{max}), because this spectroscopic parameter is in fact most readily susceptible to direct measurement. At the same time the integral absorption coefficient k and the band width $\Delta\nu$ are known to have a direct physical significance; k_{max} is related to them unambiguously; $k_{max} = Ak/\Delta\nu$, where A is a constant which depends on the units of the quantities in the expression. The factors determining the form of the $k(N)$ and $\Delta\nu(N)$ relations [and hence also of $k_{max}(N)$] are complex and numerous. In particular, one can specify tens of factors influencing the form of the function $\Delta\nu(N)$. They include, for example, the changes in density and refractive index when the microstructure is damaged[34,128], the interaction of vibrations of different types as a consequence of their anharmonicity[129,130], intermolecular interactions[128,129], the resonance of vibrations[131], a non-rigorous validity of the selection rules with respect to the phase parameter[1], polydispersity of the polymer[132], the presence of an amorphous phase and a folded structure in the polymer[34], internal stresses[133], the distribution of the paths traversed by the optical phonon with respect to length[52], band splitting under the influence of the field in the polymer crystal[34], and many others.

Table 2. Crystalinity bands.

Polymer	ν, cm^{-1}	Refs.
Orthorombic polyethylene	1894	[76]
ditto	1178	[76]
"	1050	[76]
"	731	[99,100]
Triclinic polyethylene	721	[101]
Monoclinic polyethylene	717	[83]
ditto	715	[102]
Polyisoprene	1130	[34]
Tetragonal polybut-1-ene	905	[103]
Orthorhombic polybut-1-ene	510	[103]
Hexagonal polybut-1-ene	925	[103]
ditto	1096—1098	[104,105]
"	1059—1062	[104,105]
"	1028	[104,105]
"	922—924	[104,105]
"	848	[104,105]
"	816	[104,105]
Poly(vinyl chloride)	1426	[87]
ditto	1333	[87]
"	1254	[87]
"	1229	[87]
"	957	[87]
Poly(vinylidene chloride)	884	[106]
ditto	753	[106]
Polychlorotrifluoroethylene	1285	[107,108]
ditto	580	[107,108]
Poly(ethylene terephthalate)	1685	[91]
ditto	1386	[91]
"	1130	[91]
"	1110	[91]
Poly(vinyl alcohol)	1146	[111]
Poly(n-butyl acrylate)	1255	[112]
ditto	1215	[112]
Amylose	855	[113]
Polytetrafluoroethylene	625	[89]
ditto	516	[89]
Polyoxyethylene	1283	[114]
ditto	1244	[114]
"	1236	[114]
"	1062	[114]
"	947	[114]
"	963	[114]
Orthorhombic polyoxymethylene	1488	[115]
ditto	1466	[115]
"	1237	[115]
"	1220	[115]
"	434	[115]
"	428	[115]
Trigonal polyoxymethylene	1434	[116]
ditto	1381	[116]
Orthorhombic polyesters $[-(CH_2)_m-O-]_n$ (m = 6,8,10,12)	730	[117]
Pentone	1325	[118]
Polychlorotrifluoroethylene	506	[107,108]
ditto	490	[107,108]
"	438	[107,108]
Poly(vinylidene fluoride)	1075	[109]
ditto	980	[109]
"	855	[109]
"	798	[109]
"	762	[109]
Polychloroprene	952	[110]
ditto	782	[110]
Orthorhombic polyesters $\left[-(CH_2)_m-\overset{\overset{O}{\|}}{C}-O-\right]_n$	1724	[84]
Monoclinic polyesters $\left[-(CH_2)_m-\overset{\overset{O}{\|}}{C}-O-\right]_n$	1732	[84]

Some of these factors are unimportant and in most real cases their influence can be neglected compared with the marked changes in the intensities and widths of the regularity bands (frequently by a factor of several tens) when N is altered. The influence of other factors can be reduced to a minimum by selecting the appropriate experimental conditions. Henceforth we shall deliberately restrict the range of bands considered to those for which the dependence of the intensity on the structure is not complicated by factors difficult to take into account, such as resonance. As a result, there remain a small number of factors whose influence on the $k(N)$ and $\Delta\nu(N)$ relations must be considered[43].

Table 3. Amorphous structure bands.

Polymer	ν, cm^{-1}	Refs.	Polymer	ν, cm^{-1}	Refs.
Polyethylene	1350	[121]	Pentone	1027	[119]
ditto	1340	[122]	Poly(n-butyl acrylate)	1240	[112]
»	1304	[121, 123]	ditto	1035	[112]
»	722—723	[80, 3]	Poly(ethylene terephthalate)	1580	[91]
»	1367—850	[120]	ditto	1453	[91]
Polytetrafluoroethylene	850	[125]	»	1248	[91]
ditto	778	[125]	»	1180	[91]
»	718	[125]	»	1120	[91]
»	640	[89]	»	1100	[91]
Polychlorotrifluoroethylene	755	[107, 108]	»	1042	[91]
Poly(vinylidene fluoride)	740	[109]	»	897	[91]
Polyoxymethylene	1420	[116]	»	502	[126]
ditto	1390	[116]	Polyamide-66	1329	[127]
Polyoxyethylene	1296	[114]	ditto	1224	[127]
ditto	1249	[114]	Amylose	1295	[113]
«	1038	[114]			
«	945	[114]			

1. Integral Intensity

In order to determine the dependences of the integral intensities of the longitudinal vibration bands on N, it is necessary to take into account first the dilution effect, which arises because the fraction of chain units in the vicinity of the defect have force constants and configurations somewhat different from those for units remote from the defect due to the influence of the latter. The fraction of the energy of the normal vibration corresponding to the units near the defect can then decrease sharply even for an insignificant degree of perturbation[52]. In other words, a chain with a length shorter than the actual length N is effectively involved in the longitudinal chain vibration, which leads to the following dependence of the integral absorption coefficient k on N [43]:

$$k(N) \propto 1 - N_0/N \,. \qquad (2)$$

The $k(N)$ relation for transverse vibration bands is characterised by the presence of maxima and minima. It can be shown[1,52] that in this case the following expression holds for sufficiently high values of N:

$$k(N) \propto \frac{1}{N} \cos^2 \frac{mN\pi}{n} \,, \qquad (3)$$

where n is the number of units of the macromolecule with helical symmetry, corresponding to m turns of the helix. Evidently Eqn.(3) has deep minima which repeat with a period corresponding to n units.

2. Broadening of the Bands

We shall consider initially the case of a dilute polymer solution. There are several theories explaining the broadening of the spectral bands in the liquid phase[5,128,130,134–137]. Among these, the most promising theory, yielding the best agreement with experimental data, is the fluctuation theory developed by Bakhshiev[128]. According to it, the main cause of the broadening of the bands in the spectrum of the liquid phase is the fluctuation of the microdensity of the immediate environment of the molecule.

Allowance for the influence of these fluctuations in the first-order perturbation theory in the NRCU system leads to the following dependence of the chain vibration band width on the chain length and temperature[43]:

$$\Delta\nu \propto (T/N)^{1/4} \,. \qquad (4)$$

This result is not unexpected bearing in mind that the fractional fluctuation of a physical quantity (in this case frequency) for a system consisting of N equivalent objects (in the given case units), whose fluctuations are independent, is inversely proportional to $N^{1/2}$.

The assumption of the independence of the perturbations[138] of the individual units, which is valid in the case of a solution, becomes incorrect in the general case for a polymer in bulk, for example, for a polymer crystal. In the latter case the microdensity fluctuations are caused mainly by the acoustic vibrations of the lattice and hence are to some extent correlated along the chain. The $\Delta\nu(N)$ relation must then be weaker. We shall explain this by a simple example. We shall assume that the perturbing influence of the medium is such that it leads to a synchronous change in the force constants of all the units (the case of maximum correlation). Here the fluctuations in the frequency of the macromolecule, leading to a broadening of the band, are evidently the same as for a single unit, i. e. are independent of N.

In the case of a partial breakdown of the correlation of the acoustic lattice vibrations, as a consequence of anharmonicity, it can be shown[43] that, in the terms of the first-order perturbation theory, the dependence of $\Delta\nu$ on N is

$$\Delta\nu(N) \propto \frac{T^{1/4}}{(N+1)^{3/4}} \left[\sum_{i,j,k=1}^{N} \sum_{k_t=1}^{N_t} \sin^2 \frac{i\pi}{N+1} \cdot \sin^2 \frac{j\pi}{N+1} \times \right.$$
$$\left. \times \sin \frac{ik\pi}{N+1} \cdot \sin \frac{jk\pi}{N+1} \cdot \frac{e^{-|i-j|/N_p^a}}{\omega_{kk_t}^2} \right]^{1/4} , \qquad (5)$$

where N_t is the number of chains constituting the crystal, N_p^a the characteristic length of the section of the chain participating in the correlated acoustic vibrations and having the same physical significance as the average length of the free path of the acoustic phonon, and ω_{kk_t} are the frequencies of the acoustic branch, which are defined by the following relation when account is taken of only the short-range interactions in the NCRU system:

$$\omega_{kk_t}^2 \propto \sin^2 \frac{k\pi}{2(N+1)} + \sigma \sin^2 \frac{k_t\pi}{2(N_t+1)} \,.$$

Here the parameter σ characterises the "interaction" of the oscillators of the neighbouring chains in the NCRU.

Analysis of Eqn.(5) shows that, for low values of N_p^a ($N_p^a < 10$) and high values of σ ($\sigma > 0.5$), the nature of the relation $\Delta\nu(N) \propto N^{-1/2}$ is the same as for a polymer solution [see Eqn.(4)]. Comparison of Eqn.(5) with the experimental $\Delta\nu(N)$ relations shows that this limiting case in fact usually obtains for regularity bands.

Table 4. The form of the $k_{max}(N)$ relations for regularity bands of different types.

Type of vibration	Local vibrations of terminal defects, "contacts", etc.	Characteristic vibrations of repeating units;	Chain vibrations; $N_p^0 \lesssim 1$		
			$\omega(N)$=const		$\omega(N) \neq$ const
			longitudinal	transverse	
$N_p^a \gg 1$ (macromolecule in crystallite)	$k_{max} \sim N^{-1}$ $N \gg 1$	$k_{max}(N)$=const $N > N_p^0$	$k_{max} \sim 1 - N_0/N$ $N < N_0$	$k_{max} \sim \cos^2(\pi mN/n) \cdot N^{-1}$ $N \gg N_0$	Spectral curve has a complex contour
$N_p^a \lesssim 1$ (macromolecule in solution)	$k_{max} \sim N^{-1}$ $N \gg 1$	$k_{max}(N)$=const $N > N_p^0$	$k_{max} \sim N^{1/2}(1 - N_0/N)$ $N_0 < N < N_p^0$	$k_{max} \sim \cos^2(\pi mN/n) \cdot N^{-1/2}$ $N > N_0$	

We may note that a marked breakdown of the correlation of perturbations can then be favoured not only by the anharmonicity of the acoustic vibrations but also by the stationary breakdown of the regularity of the immediate environment of the macromolecule (non-ideality of the crystal structure, defects of the neighbouring molecules, etc.).

3. The Intensities at the Regularity Band Maxima

It follows from Eqns.(2) and (4) that, for longitudinal vibration bands, we have:

$$k_{max}(N) \propto N^{1/2}(1 - N_0/N) \quad . \qquad (6)$$

We may note that Eqns.(4)–(6) do not take into account the finite length of the free path of the optical phonon N_p^0 which amounts for certain regularity bands, as will be shown below, to several tens of units and can be estimated from the value of N for which the experimental $\Delta\nu(N)$ and $k_{max}(N)$ relations deviate from those defined by Eqns.(4)–(6).

VI. CLASSIFICATION OF THE INFRARED BANDS OF POLYMERS

After the principal mechanisms of the influence of the length of the regular segments in macromolecules on the intensities and widths of the infrared bands have been elucidated, it is possible to isolate, within the framework of the cluster approach, groups of bands differing in the nature of the dependence of their absorption coefficients on the length of the segment.

Several attempts have been made at a classification of the structure-sensitive bands in the infrared spectra of polymers, which, however, are only qualitative[50,74]. Our proposed classification is based on the type of dependence of the frequency ω and the absorption coefficient at the band maximum k_{max} on the length of the regular segment N. According to this classification, it is possible to isolate in the infrared spectrum bands which can be more or less definitely assigned to one of the types of vibration of the macromolecular chain: local, characteristic, or chain. In order to make this classification more informative and clearer, we also introduced into consideration parameters characterising the lengths of the paths of the phonons of the optical vibration considered (N_p^0) and the low-frequency acoustic vibrations (N_p^a) with which the given optical vibration interacts. The types of the $k_{max}(N)$ relations and the corresponding values of N_0, N_p^0 and N_p^a as well as the ranges in which N varies and the band polarisations are given in Table 4.

We shall consider the problem of the kind of information about the structure of the polymer contained in each band type. The bands due to the local vibrations of the defects ($k_{max} \propto N^{-1}$) can be used to determine the nature and concentration of the defects, particularly the "contacts" between blocks of different kinds and hence the number-average sequence length or the number-average molecular weight in the case of oligomers.

The characteristic bands of the chain vibrations ($N_p^0 \lesssim 1$, $k_{max} \cong$ const.) can be used to determine the chemical, isomeric, and conformational compositions of the polymers.

The $k_{max}(N)$ relation for the transverse vibration bands at $N_p^0 \gg 1$ contains information about the nature of the helical symmetry of the regular section of the chain (parameters m and n). However, such bands are unsuitable for the determination of the average length $\bar{N}$ of the regular segments as a consequence of the non-monotonic $k_{max}(N)$ relation.

The longitudinal vibration bands for $N_p^0 \gg 1$ and $N_p^a \lesssim 1$, for which there is a strong monotonic dependence of k_{max} on N defined by Eqns.(6), are the most suitable for the determination of the average length of the regular segments in macromolecules. As mentioned above, when these bands are used, the question of the nature of the averaging of the length arises.

VII. THE REGULARITY BANDS AND THE DISTRIBUTION OF THE REGULAR SEGMENTS IN MACROMOLECULES WITH RESPECT TO LENGTH

In conformity with the cluster approximation, each segment makes an independent contribution to the integral absorption coefficient at the specified frequency. Taking this fact into account as well as Eqn.(2), it is easy to obtain an expression for the absorption coefficient of the specimen in terms of the distribution function with respect to the lengths of the segments $w(N)$:

$$k(\bar{N}) \propto \sum_{N=N_0}^{\infty} w(N) \cdot \left(1 - \frac{N_0}{N}\right) \quad .$$

On the other hand, by measuring the optical density of a specimen with an unknown distribution function and using Eqn.(2) as the calibration relation, we obtain

$$1 - \frac{N_0}{\bar{N}} = \sum_{N=N_0}^{\infty} w(N) \cdot \left(1 - \frac{N_0}{N}\right) \quad ,$$

whence

$$\bar{N} = \left(\sum_{N=N_0}^{\infty} \frac{w(N)}{N} \right)^{-1} \equiv \bar{N}_n \quad .$$

Consequently *the integral absorption coefficient of the regularity band contains information about the number-average length of the regular segments.*

The dependence of the absorption coefficient at the regularity band maximum on the function $w(N)$ can be analysed analogously[43]. It follows from Eqn.(6) that

$$k_{max}(\bar{N}) \propto \sum_{N=N_0}^{\infty} w(N) \cdot N^{1/2}\left(1 - \frac{N_0}{N}\right) \quad . \qquad (7)$$

Analysis of Eqn.(7) shows that, for relatively high values of N (for $N \gg N_0$), the square of the experimental optical density is proportional to $\bar{N}_1$ defined by the relation

$$\bar{N}_1 = \left[\sum_{N=N_0}^{\infty} w(N) \cdot N^{1/2}\right]^2 \quad .$$

On the other hand, if values of N in the range $N_0 \leqslant N < 2N_0$ are characteristic of the main bulk of the polymer molecules, the optical density is proportional to $\bar{N}_2$:

$$\bar{N}_2 = \sum_{N=N_0}^{\infty} [w(N)N] - N_0 \equiv \bar{N}_w - N_0 \quad .$$

In the general case the following relation holds for the "spectroscopic average" length $\bar{N}_S$:

$$\bar{N}_n < \bar{N}_1 \leqslant \bar{N}_s \leqslant \bar{N}_2 < \bar{N}_w \quad .$$

where $\bar{N}_n$ and $\bar{N}_w$ are the number-average and the weight-average lengths of the regular segments respectively.

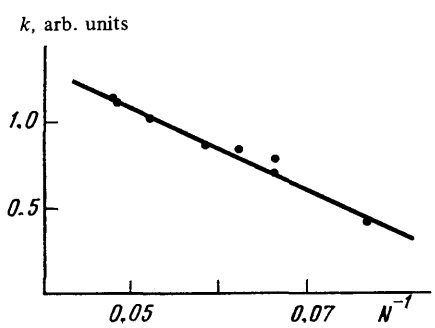


Figure 3. Dependence k on N^{-1} for the wagging vibration band (720 cm^{-1}) of orthorhombic n-paraffins at 173 K.[43]

Thus *the average length of the regular segments in macromolecules determined from the absorption coefficient at the regularity band maximum lies in the range between the number-average and weight-average lengths and usually approaches the latter.*

Finally we may note that the ratio of the average lengths of segments measured on the basis of the peak and integral regularity band intensities $\bar{N}_S/\bar{N}_n$ characterises the width of the distribution $w(N)$.[52,139]

VIII. SOME EXAMPLES OF STUDIES ON THE MICROSTRUCTURES OF POLYMERS WITH THE AID OF REGULARITY BANDS

Since regularity bands can belong to one type or another indicated in Table 4, the dependence of their parameters (k_{max} and $\Delta\nu$) on N (or on T) should have different linearising coordinates defined by Eqns.(2), (4), and (6). We shall quote several typical examples of experimental relations of this kind.

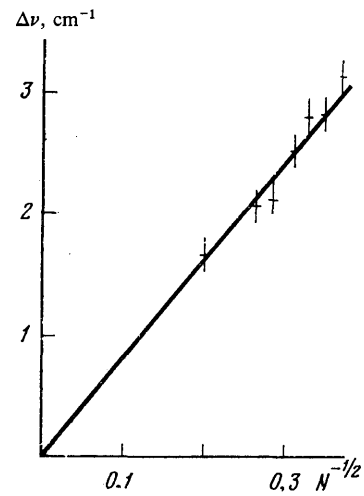


Figure 4. Dependence of $\Delta\nu$ on $N^{-1/2}$ for the forbidden band of the wagging-torsional vibrations of triclinic n-paraffins (735–770 cm^{-1}) at 100 K.[43]

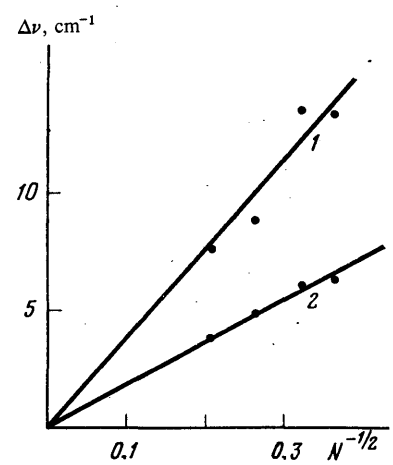


Figure 5. Dependence of $\Delta\nu$ on $N^{-1/2}$ for the C–O stretching vibration and CH_2 wagging vibration bands (845 cm^{-1}, line *1*) and the fanwise CH_2 vibrations (1346 cm^{-1}, line *2*) of the urethanes C_4H_9–NH–CO–O–$(CH_2$–CH_2–O$)_N$–CO–NH–C_4H_9 at 100 K.[52]

Fig. 3 shows that the coordinates (k, N^{-1}) [see Eqn. (2)] are linearising for the band due to the wagging vibrations of n-paraffins.

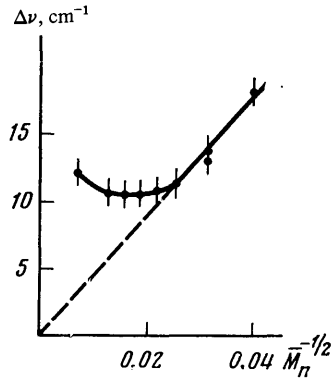


Figure 6. Dependence of $\Delta\nu$ on $\bar{M}_n^{-1/2}$ for the 845 cm^{-1} band in the spectra of crystalline poly(ethylene glycols) at 10 °C.[43]

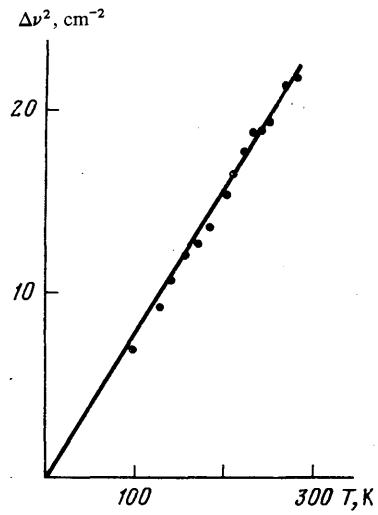


Figure 7. Dependence of $\Delta\nu^2$ on T for the wagging vibration band (720 cm^{-1}) of triclinic n-tetradecane.

When the correlation of the acoustic vibrations undergoes a pronounced distortion in conformity with Eqn. (4), the coordinates $(\Delta\nu, N^{-1/2})$ are also linearising, provided that the chain length does not exceed the length of the free path of the optical phonon N_p^0. Figs. 4 and 5 show that, for not unduly high values of N, the plots of $\Delta\nu$ against $N^{-1/2}$ for certain regularity bands in the spectra of polymers containing polymethylene and polyoxyethylene segments are straight lines passing through the origin of coordinates. The deviation from Eqn. (4) in the case of the 845 cm^{-1} band of poly(ethylene glycols) with molecular weights $\bar{M}_n > 2000$ (Fig. 6) can be accounted for by the finite length of the free path of the optical phonon as a consequence of the anharmonicity of the vibrations or the appearance of a folded structure.

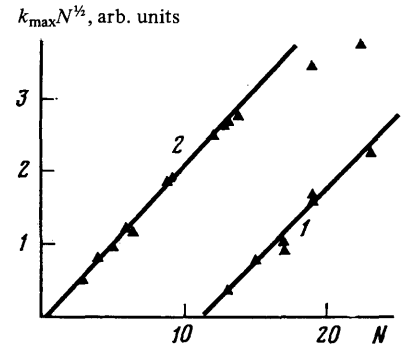


Figure 8. Dependence of $k_{max}N^{1/2}$ on N for different bands: *1*) wagging vibrations (720 cm^{-1}) of orthorhombic n-paraffins at 170 K;[52] *2*) torsional vibrations (1283 cm^{-1}) of glymes, poly(ethylene glycols), and epoxyethane-expoxypropane copolymers at 170 K.[48]

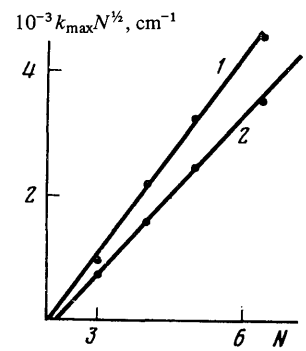


Figure 9. Dependence of $k_{max}N^{1/2}$ on N for the fanwise vibration (1350 cm^{-1}) (line *1*) and torsional vibration (1285 cm^{-1}) (line *2*) bands of glymes and poly(ethylene glycol) with $\bar{M}_n = 300$ at 180 K;[48] solvent-carbon disulphide.

The temperature variation of the regularity bands considered is also described by Eqn. (4). An example of such a relation is presented in Fig. 7.

According to Eqn. (6), the dependence of $k_{max}N^{1/2}$ on N should be linear under the condition $N_p^a \leq 1$ and $N < N_p^0$. The linearity of this relation has been observed for a series of regularity bands of polymers containing polymethylene, polyoxyethylene, and polystyrene sequences of units in the crystalline state and in the form of solutions at low temperatures (see, for example, Figs. 8–10).

However, in some cases the hypothesis of a pronounced distortion of the correlation of perturbations along the chain and Eqns. (4) and (6) derived on this basis do not allow a

satisfactory description of the $k_{max}(N)$ relation. For example, such relations for certain structure-sensitive bands in the spectra of compounds containing polyoxybutylene and polystyrene sequences of units can be described only with the aid of the exact Eqn.(5) for the band width with the optimised parameters N_p^a, σ, and N_0 (Figs.11–13).

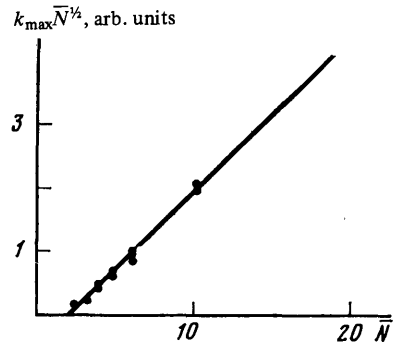


Figure 10. Dependence of $k_{max}\bar{N}^{1/2}$ on $\bar{N}$ for the 1053 cm^{-1} band of the isotactic crystalline styrene–styrene-α-d_1 copolymer[37] ($\bar{N}$ is the average length of the polystyrene segment).

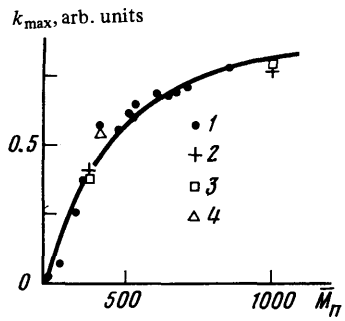


Figure 11. Dependence of k_{max} for the 565 cm^{-1} band on the number-average molecular weight of the polyoxybutylene block for low-temperature solutions in carbon disulphide; *1*) of oligomeric fractions of polytetrahydrofuran; *2*) of initial oligomers; *3*) of acetylated oligomers; *4*) of the tetrahydrofuran–epoxypropane block copolymer[47]. The continuous curve has been calculated by Eqn.(5) with the optimised values of the parameters N_p^a and σ.

1. Analysis of the Helical Structure of Polymer Chains

The bands of transverse vibrations with fairly high values of N_p^0 ($N_p^0 > 2n$, see Table 4) are sensitive to the type of helical symmetry. In order to determine the parameter n of the helix, it is desirable to use bands which correspond to low values of N_p^a; for such bands, the amplitude of the oscillations in the $k_{max}(N)$ relation does not decay unduly rapidly.

In the case of polymethylene chains whose skeleton has a planar zigzag conformation and hence the helical symmetry 2_1 (i.e. two units per turn of the helix), an alternation (with a period of two units) of maxima and minima in the $k_{max}(N)$ curve is to be expected for the transverse vibration bands. Such alternation has indeed been observed for a series of n-paraffins in the region of torsional vibrations (950–1060 cm^{-1}), since the bands corresponding to these vibrations are absent from the spectra of molecules containing an odd number of carbon atoms[124]. For polymers containing regular polyoxyethylene segments with narrow distribution functions with respect to their lengths, the period of the oscillations of the corresponding experimental $k(N)$ relation is equal to seven units (Fig.14). This finding is in good agreement with X-ray diffraction data[140], according to which the polyoxyethylene chain consists of a 7_2 helix.

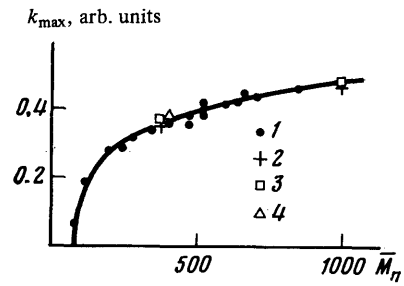


Figure 12. Dependence of k_{max} for the 750 cm^{-1} band in the spectra of low-temperature solutions of model compounds (for legend, see Fig.11) in carbon disulphide on the number-average length of the polyoxybutylene block[47].

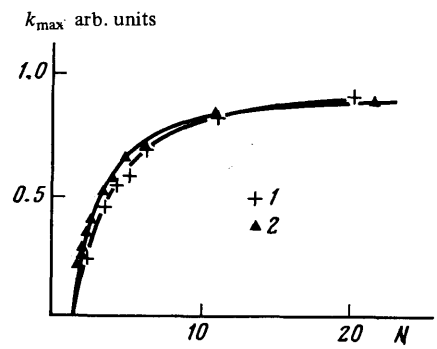


Figure 13. Dependence of k_{max} on the average length of the polystyrene segment for the 1194 cm^{-1} band of the isotactic styrene–styrene-α-d_1 copolymer; *1*) solution in carbon disulphide at −104 °C; *2*) crystalline specimens[37]. The continuous curves have been calculated by Eqn.(5) with optimised values of the parameters N_p^a and σ.

2. The Sequence Length of Tetrahydrofuran-Epoxypropane Copolymers

The structures of such copolymers have been analysed only for polyoxybutylene blocks[47]. Table 5 presents the average lengths $\bar{N}$ of these blocks in copolymers of different composition determined with the aid of the curves illustrated in Figs. 11 and 12. Table 5 also presents the number-average ($\bar{N}_n$) and weight-average ($\bar{N}_w$) lengths calculated from kinetic data[141]. As was to be expected, the lengths determined by the spectroscopic method have intermediate values.

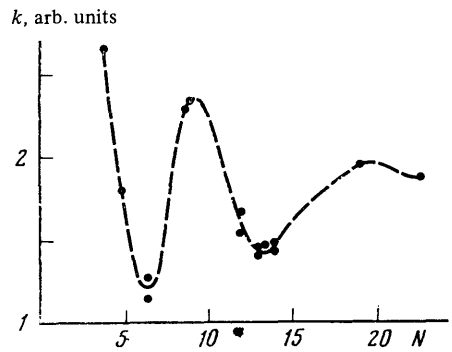


Figure 14. Dependence of k on the length of the polyoxyethylene segment for the 1366 cm^{-1} band in the spectra of glymes, poly(ethylene glycols), and epoxyethane–epoxypropane copolymers at −100 °C.[43]

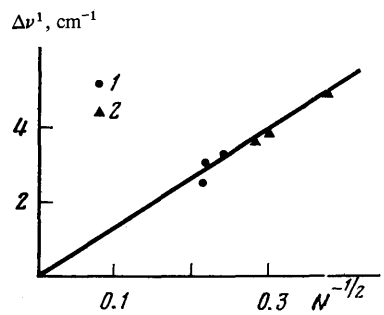


Figure 15. Dependence of the width of the high-frequency wing of the wagging vibration band (730 cm^{-1}) in the spectra of the crystalline component of n-paraffins (1) and ethylene–but-1-ene copolymers (2) on the length of the polymethylene segment[43].

3. The Sequence Length of Epoxyethane–Epoxypropane Copolymers

The Pluronic block copolymers of epoxyethane and epoxypropane (Wyandotte Chemical Co), whose compositions, degrees of block structures, and molecular weights are rigorously correlated with one another, are convenient for testing the spectroscopic method for the analysis of the sequence length. In order to measure the average lengths of the polyoxyethylene POE segments, the dependence of the 1283 cm^{-1} bend intensity on the length of the POE block was used (Fig. 8). Table 6 presents the average lengths of the POE segments measured spectroscopically and determined from the data provided by the Company. Evidently an entirely satisfactory agreement was obtained between these quantities.

Table 5. The lengths of the PTHF sequences in tetrahydrofuran–epoxypropane (EP) copolymers[47].

THF:EP*	$\bar{N}_w$**	$\bar{N}_n$**	$\bar{N}$
1:2	2.2	1.8	2.05
1:1	2.6	2.2	2.5
2:1	3.1	2.4	2.85

* The ratio of the mole fractions of the THF and EP units in the copolymer.

** Kinetic data[141].

Table 6. The lengths of polyoxyethylene (POE) segments in epoxyethane-epoxypropane block-copolymers (Pluronic)[48].

Brand	Average length of POE block	
	Company's data	spectroscopic data
PL-44	9.1	8.8
PL-61	2.2	1.7
PL-62	5.0	4.8
PL-64	12.8	13.7
PL-72	5.9	6.1

4. The Degree of the Block Structure of Ethylene-But-1-ene Copolymers

The development of a method for the measurement of the lengths N of polymethylene blocks is of practical importance in connection with the necessity to investigate the structures of branched polyethylenes. The copolymers of ethylene with other α-olefins can be regarded as models of such polyethylenes.

Fig. 15 shows that the dependence of the half-width of the 730 cm^{-1} band on $N^{-1/2}$ for crystalline copolymers and n-paraffins is described by a single straight line passing through the origin of coordinates, in conformity with Eqn. (4) and the cluster model[43]. The spectra of the crystalline component of the copolymer were obtained by the method of compensations spectroscopy; the spectrum of the polymethylene blocks of the amorphous part of the copolymer was modelled by the spectrum of liquid pentadecane.

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In conclusion we may note that we did not mention in this review all the possibilities for structural studies which can be formulated in a wider analysis of regularity bands. For example, one can point to the method based on the analysis

of the temperature variation of the regularity band intensities—the so-called low-temperature spiralisation method[52], which makes it possible to obtain information about the distribution of regular sequences of monomeric units with respect to lengths. Unfortunately, the limited size of the review did not allow us to consider the advantages of the method of analysis using the contour of a complex spectral band whose components are the bands of chain vibrations with frequencies sensitive to the lengths of the regular segments[1,32].

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Copolymerisation of Unsaturated Organophosphorus Monomers

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The present state of the problem of the copolymerisation of unsaturated organophosphorus monomers is considered. Quantitative data on their reactivities in the radical polymerisation processes are surveyed and analysed critically, the place of these monomers among other types of unsaturated compounds is defined, and the organophosphorus monomers most promising from the standpoint of the modification of polymeric materials by copolymerisation methods are specified. The review is based on data published up to the end of 1978.
The bibliography includes 132 references.

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I. INTRODUCTION

Heat resistance, to which much attention is devoted nowadays, strong adhesion, and the formation of complexes, ion-exchange, and other properties are responsible for the interest in the practical applications of organophosphorus polymers[1]. The majority of polymers of industrial importance burn in air, which constitutes a serious obstacle to their wider and more comprehensive application. Although the introduction of fire-proofing agents into polymers is not able to prevent completely the decomposition of organic polymers on contact with flames, nevertheless it diminishes significantly the rate of propagation of the flame and can even lead to the formation of a self-extinguishing material. The best effect is achieved when chemically active fire-proofing agents[2], particularly organophosphorus monomers (OPM), are used; here the combustion-retarding agent is introduced into the polymer chain, i.e. is an integral part of the polymer. The simplest and most effective method of constructing such a chain involves the copolymerisation of OPM with other unsaturated monomers. Numerous communications devoted to the copolymerisation of unsaturated OPM including reviews and monographs[3-5], have been published hitherto, but the latest review[5] is already more than 10 years old.

Apart from purely practical applications, the copolymerisation method is of interest because it permits a quantitative estimate of the relative reactivities of monomers and polymeric radicals and makes it possible to obtain valuable information for the determination of the mechanisms of radical reactions. Whereas kinetic studies on the homopolymerisation of OPM are as yet restricted to a narrow range of monomers[6-9], the quantitative data on copolymerisation, from which correct conclusions about the influence of the structure of the OPM on their reactivity can be drawn, are fairly extensive. In the present review an attempt is made to survey and interpret critically data on the copolymerisation of OPM precisely from this point of view.

Mainly radical copolymerisation is considered, since problems of the ionic copolymerisation of the OPM have so far been dealt with only in isolated reports[10-12], where it is concluded that the vinyl derivatives of phosphorus have a very low reactivity in anionic and ionic-coordination copolymerisation. Qualitative information about the copolymerisation of unsaturated OPM is discussed only when necessary. The semivinyl copolymerisation of derivatives of tricoordinate phosphorus has been described in a recent review[13]; The semivinyl polymerisation of OPM with SO_2 is dealt with by Faizullin et al.[14]. The properties and applications of the phosphorus-containing copolymers formed will not be considered in this review, since independent reviews have been devoted to these problems[2,15-18].

The polymerisation and copolymerisation of unsaturated OPM lead to carbochain polymers with the phosphorus in the side chain. Depending on the relative positions of the phosphorus atom and the double bond and also on the reactivity of the monomer, it is useful to divide all OPM into four types (typical examples are indicated below; X = OH, OAlk, OAr, NR_2, Alk, Ar, $CH_2=CH$, etc.).

A. OPM with the phosphorus atom linked directly to a vinyl or substituted vinyl group:

$$CH_2=CHP(O)X_2,\ CH_2=C(R)-P(O)X_2,\ CH_2=CHPX_2\ .$$

B. OPM with a diene group at the phosphorus atom:

$$CH_2=CH-CH=CHP(O)X_2,\ CH_2=CP(O)X_2-CH=CH_2\ ,$$
$$CH_2=CP(O)X_2-CP(O)X_2=CH_2\ .$$

C. OPM with the phosphorus atom linked by a double bond via oxygen, nitrogen, a methylene group, or their combination:

$$CH_2=CHOP(O)X_2,\ CH_2=CH-CH_2P(O)X_2,\ CH_2=CH-CH_2OP(O)X_2\ .$$

D. OPM with the phosphorus atom remote from the double bond:

$$CH_2=CHC(O)-OCH_2P(O)X_2,\ CH_2=CH-C_6H_4-P(O)X_2\ .$$

Not only the copolymerisation but also the homopolymerisation of OPM proceeds in very different ways depending on the type to which they belong. When the phosphorus atom is fairly remote from the C = C bond (type D), polymers with a high molecular weight are obtained; no significant differences associated with the influence of the phosphorus atom are observed, since we are virtually dealing only with the polymerisation of styrene, acrylate, etc. If the phosphorus atom is attached directly to the double bond or is separated from it by an oxygen atom (types A and C), polymers with a low molecular weight are obtained owing to specific chain transfer processes, for the explanation of which a number of schemes have been proposed[6,19-22]. When the allyl group is

present in the monomer (type C), the characteristics of allyl polymerisation become of primary importance, which also leads to oligomers. The polymerisation of 1,3-diene OPM (type B) yields polymers[23,24] or copolymers[22,25] with a high molecular weight, depending on their structure.

Organophosphorus monomers undergo copolymerisation virtually with all the usual vinyl monomers, but the yields and molecular weights of the copolymers in most cases decrease with increasing content of OPM units in the macrochain[6,22,37,38]. However, when comparatively small amounts of the phosphorus-containing monomer are used, it is possible to achieve high yields of copolymers with a sufficient phosphorus content to impart to them useful properties and to achieve a satisfactory molecular weight. The introduction of small amounts of phosphorus frequently imparts to polymers new valuable qualities without a significant impairment of their physicomechanical properties. The modification of the known polymers by small amounts of phosphorus is therefore at present of greater practical interest than the synthesis of new organophosphorus polymers.

The Alfrey–Price $Q-e$ scheme is most widely used to characterise the behaviour of monomers in radical copolymerisation reactions. In the present review the parameters Q and e for OPM have been recalculated using Greenley's recently published[26] average values of $\bar{Q}-\bar{e}$ for comonomers, which have been determined by the method of least squares taking into account the probable errors in the determination of the copolymerisation constants. In certain cases Greenley's values differ significantly from the "average" values found by Young[27] and usually employed. Furthermore, in many instances we corrected the values of Q and e for the OPM because sometimes[28-30] the authors of the original communications gave preference to chemically less reasonable values of e of the two possible ones in the solution of the quadratic Alfrey–Price equation. For those compounds where this was possible, we also calculated the average parameters Q and e from the Lüssi equation[31] using Greenley's[26] criterion (the subdivision of monomers into groups based on the degree of reliability, the use of at least three–four independent determinations of the constants r_1 and r_2 for copolymerisation with comonomers belonging to a group which is not below Greenley's group III). In addition we believe it is necessary to use data for not less than three comonomers and to exclude from consideration systems with acid components†, since all the OPM discussed in this review form strong hydrogen bonds with them[32]. In the Tables below Greenley's groups are denoted by Roman numerals, n is the number of independent determinations of r_1 and r_2 used for the calculation, and R is the correlation coefficient. We emphasize that in the case of OPM the use of the Lüssi equation is particularly convenient, since this equation does not include the copolymerisation constants r_1 referring to the phosphorus-containing macroradical, which are as a rule determined with a lower relative accuracy than the constants r_2 referring to the comonomer macroradical. Furthermore, systems with r_1, $r_2 > 1$ and $r_1 = 0$ can be used to calculate $\bar{Q}$ and $\bar{e}$ by the Lüssi–Greenley method.

The following abbreviations have been adopted in this review: (1) for the names of organic monomers: AA = acrylic acid, AN = acrylonitrile, VA = vinyl acetate, VDC = vinylidene chloride, VC = vinyl chloride, DMA = dodecyl methacrylate, MA = methyl acrylate, MAA = methacrylic acid, MAn = maleic anhydride, MVP = 2-methyl-5-vinylpyridine, MMA = methyl methacrylate, and St = styrene; (2) for the names of organophosphorus monomers (OPM): VP = vinylphosphonate(s), MPB = monophosphonobutadiene(s), DPB = diphosphonobutadiene(s), VPA = vinylphosphonic acid $CH_2=CHP(O)(OH)_2$, DMVP = dimethyl vinylphosphonate $CH_2=CHP(O)(OCH_3)_2$, DCVP = di-β-chloroethyl vinylphosphonate $CH_2=CHP(O)(OCH_2CH_2Cl)_2$, DEVP = diethyl vinylphosphate $CH_2=CHP(O)(OC_2H_5)_2$, DEIP = 1-diethylphosphono-2-methylbuta-1,3-diene $CH_2=CH-C(CH_3)=CHP(O)(OC_2H_5)_2$, DEMOP = diethyl α-methacryloyloxymethylphosphonate $CH_2=C(CH_3)C(O)-OCH_2P(O)(OC_2H_5)_2$, DEIPO = 1-(diethylphosphine oxide)-2-methylbuta-1,3-diene $1,3\text{-}CH_2=CH-C(CH_3)=CHP(O)(C_2H_5)_2$, DEPB = 2,3-bis(diethylphosphono)buta-1,3-diene $CH_2=C[P(O)(OC_2H_5)_2]-C[P(O)(OC_2H_5)_2]=CH_2$, TMDVP = tetramethyldiaminovinylphosphonate $CH_2=CHP(O).[N(CH_3)_2]_2$, TEDIP = 1-bisdiethylaminophosphono-2-methylbuta-1,3-diene $CH_2=CH-C(CH_3)=CHP(O)[N(C_2H_5)_2]_2$, and α-PVPA = α-phenylvinylphosphonic acid $CH_2=C(C_6H_5)-P(O)(OH)_2$.

II. MONOMERS WITH THE PHOSPHORUS ATOM AT A VINYL GROUP (TYPE A)

This class includes mainly derivatives of vinylphosphonic acid, vinylphosphines, and phosphine oxides (Table 1). The greatest amount of data has been obtained for the copolymerisation of vinylphosphonate esters.

The influence of the nature of the substituents at the phosphorus atom on the activity of VP can be traced in systems with St and VA. In relation to both polystyrene and poly(vinyl acetate) radicals, VP can be arranged in the following sequence in terms of their reactivities: DCVP > DMVP > DEVP, i.e. the reactivity of the OPM increases with the increasing electronegativity of the ester groups. The polymeric St and VP radicals add more readily to St and the poly-VA radical adds more readily to VP than to its own monomer: as a result, St is incorporated more effectively in the polymer chains than the OPM and VA and OPM have on the whole comparable reactivities in copolymerisation, but VP are nevertheless somewhat more reactive ($r_1 > r_2$).

Examination of the copolymerisation constants for the vinyl OPM together with the known copolymerisation constants for monomers without phosphorus[51] makes it possible to set up reactivity series for these monomers in relation to various macroradicals[38]. In relation to both polystyrene and poly(vinyl acetate) radicals, VP exhibit a reactivity which is intermediate between those for the conjugated (MA) and non-conjugated (VA) monomers with analogous structures. It is of interest that the reactivity of TMDVP does not differ from that of esters in relation to the polystyrene macroradical[38], which has also been noted for the addition of the phenyl radical[52].

The data in Table 1 make it possible to arrange monomers in the following sequence in terms of their reactivities with respect to the poly-DEVP radical ($1/r_1$): VA < AN < MAA < MA ≤ St < MMA. This series agrees on the whole with the series for the usual organic macroradicals[53], which shows that the behaviour of polymeric phosphorus-containing radicals in copolymerisation reactions is similar to that of ordinary macroradicals.

In addition, the copolymerisation constants together with the elementary chain propagation constants for OPM [7,8] and other monomers[53] make it possible to estimate the constants k_{21} for the addition of various radicals to the same OPM.[38] The reactivity of a phosphorus-containing macroradical may be comparable to that of the relatively inactive polystyrene

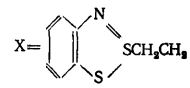
† The copolymerisation constants for the diethyl vinylphosphonate–acrylic acid system depend greatly on the nature of the solvent[33].

radical in the reaction involving addition to vinylphosphonates, while the large difference between the values of r_1 and r_2 in systems with St is almost exclusively caused by the high rate constants for the homoaddition of St and the low reactivity of VP as monomers. On the whole, some tendency towards a higher rate of addition of macroradicals to the dimethyl ester compared with the diethyl ester is observed[38].

Table 1. The copolymerisation constants for vinylphosphonic acid and its derivaties $CH_2=CHP(O)X_2$ (M_2) and the Alfrey–Price parameters.

M_2	t, °C	r_1	r_2	$1/r_2$	Refs.	e_2	Q_2
			X=HO				
St	60	0.13±0.02	24±1	0.04	[34]	—	—
MMA	60	0.09±0.01	5.6±1	0.18	[34]	1.21	0.18
AA	60	0.30±0.05	8±1	0.13	[35]	—	—
MAA	60	0.15±0.02	6±1	0.17	[35]	0.91	0.28
			X=Cl				
St	−78	0.097	1.6	0.63	[36]	0.56	0.21
MMA	−78	0.081	2.1	0.48	[36]	1.71	0.59
MMA	25	0.084	6.6	0.15	[36]	1.15	0.15
			X=CH_3O *				
St	60	0.40±0.17	4.61±0.43	0.22	[37]	—	—
St	60	0.015±0.01	5.46±0.37	0.18	[38]	0.78	0.05
VA	60	0.82±0.09	0.06±0.01	16.67	[38]	0.89	0.12
AN	—	0.09±0.02	3.55±0.18	0.28	[39]	2.31	0.51
DEVP	60	1.04±0.06	1.07±0.03	0.93	[38]	—	—
			X=C_2H_5O **				
St	—	0	3.25	0.31	[19]	—	—
St	60	0	4.40±0.50	0.24	[37]	—	—
St	60	0.06±0.02	6.32±0.34	0.16	[38]	0.19	0.07
St	—	0.06±0.02	8.87±0.14	0.11	[40]	0.01	0.21
VA	60	0.74±0.13	0.09±0.03	11.11	[38]	0.81	0.09
AA[a]	100	0.48±0.07	1.92±0.14	0.52	[33]	1.17	0.84
AA[b]	100	0.26±0.05	1.36±0.07	0.73	[33]	1.90	2.36
AA[c]	100	0.47±0.10	2.37±0.27	0.42	[33]	—	—
AA[d]	100	0.21±0.02	3.80±0.03	0.26	[33]	1.36	0.50
MA	60	0.06±0.03	6.82±0.16	0.15	[38]	1.54	0.11
AN	—	0.20±0.10	4.80±0.16	0.21	[39]	1.44	0.13
MAA	60	0.15±0.15	1.90±0.50	0.53	[41]	1.71	1.40
MMA	70	0.04±0.02	11.2±0.20	0.09	[131]	1.27	0.09
Ethylene	80	0	0.17±0.03	5.88	[42]	—	—
DMVP	60	1.07±0.03	1.04±0.06	0.94	[38]	—	—
			X=$ClCH_2CH_2O$ ***				
St	60	0.2±0.2	2.2±0.4	0.45	[43]	0.11	0.22
St	50	0.03	2.43	0.41	[44]	0.82	0.11
St	30	0.16	2.30	0.43	[45]	0.20	0.20
St	60	0.18±0.05	2.45±0.06	0.41	[38]	0.10	0.20
VA	60	0.85±0.06	0.04±0.01	25.0	[38]	1.0	0.17
MAA	60	0.10±0.08	1.7±0.5	0.59	[43]	1.92	1.78
MAA[e]	60	0.05	3.5	0.29	[46]	1.91	0.86
MAA[b]	60	0.01	4.5	0.22	[46]	1.48	0.52
MMA	30	0.26	29.9	0.03	[45]	—	—
VC	60	1.16±0.15	0.52±0.04	1.92	[47]	0.91	0.12
Ethylene	160	2.7	0.04	0.37	[48]	1.47	0.29
DEMOP	70	0.15±0.09	1.35±0.22	0.74	[49]	—	—
DEIP	70	0.15±0.08	2.12±0.04	0.47	[49]	—	—
TEDIP	70	0.10±0.10	2.0±0.4	0.50	[49]	—	—
DEIPO	70	0.06±0.06	2.86±0.10	0.35	[49]	—	—
DEPB	70	0.10±0.05	1.00±0.15	1.0	[49]	—	—
			X=C_3H_7O				
St	60	0.90±0.09	4.24±1.04	0.24	[37]	—	—
AN	40—90	0.20±0.24	4.60	0.22	[50]	1.53	0.15
			X = iso-C_3H_7O				
St	60	0	2.39±0.37	0.42	[37]	—	—
AN	40—90	0.50±0.53	4.5	0.22	[50]	—	—
			X=C_4H_9O ****				
St	60	0,3±0.3	5.4±1.5	0.19	[37]	—	—
AN	40—90	0.3—0.32	4.90	0.20	[50]	—	—
Ethylene	160	0	2.5	0.40	[48]	—	—
			X = iso-C_4H_9O *****				
St	60	0.5±0.4	4.4±1.0	0.23	[37]	—	—
AN	40—90	0.20—0.27	4.70—4.76	0.21	[50]	—	—
Ethylene	160	0	1.7	0.59	[48]	—	—
			X = iso-$C_5H_{11}O$				
AN	40—90	0.10—0.08	5.7	0.18	[50]	1.99	0.21
			X=C_6H_5O				
St	60	0	2.03±0.39	0.49	[37]	—	—
MAA[e]	60	0.13	3.5	0.29	[28]	1.48	0.67
Ethylene	80	0	0.11±0.02	9.09	[42]	—	—

Table 1. (cont.)

M_2	t, °C	r_1	r_2	$1/r_2$	Refs.	e_2	Q_2
			X=p-ClC_6H_4O				
MAA[e]	60	0.25	2.8	0.36	[28]	1.19	0.70
			X=p-$NO_2C_6H_4O$				
MAA[e]	60	0.40	1.9	0.53	[28]	1.11	1.0
			X=o-$NO_2C_6H_4O$				
MAA[e]	60	0.20	3.1	0.32	[28]	1.28	0.67
			X= 				
VC	60	0.07±0,06	3,89±0.08	0.26	[29]	1.36	0.02
			X=$(CH_3)_2N$				
St	60	0±0.02	6.20±0.24	0.16	[38]	0.65	0,05

Remarks: Solvents: [a]benzene, [b]dioxan, [c]ethyl methyl ketone, [d]water, and [e]DMF. Copolymerisation parameters and Greenley groups: $*\bar{e}_1=0.82$, $\bar{Q}_1=0.10$ (group IV, $n=5$, $R=0.92$); $**\bar{e}_1=0.92$, $\bar{Q}_1=0.074$ (group III, $n=6$, $R=0.99$); $***\bar{e}_1=1.59$, $\bar{Q}_1=0.07$ (group III, $n=7$, $R=0.91$); $****\bar{e}_1=0.62$, $\bar{Q}_1=0.03$ (group V, $n=3$, $R=0.28$); $*****\bar{e}_1=0.66$, $\bar{Q}_1=0.03$ (group V, $n=3$, $R=0.43$).

In all the systems (with the exception of AA and MAA) the parameters Q for the vinylphosphonate esters are similar and the electronegativity factors e (Table 1) vary within wide limits depending on the nature of the comonomer. For example, the shape of the curve representing the composition of the copolymers in the systems with St, MA, and MMA cannot therefore be predicted even qualitatively from the values of Q and e for the systems with VA, which is also characteristic of butyl vinylsulphonate[54], structurally similar to VP, and a number of other organoelemental monomers[55-57].

In contrast to the foregoing, when the values of $\bar{Q}$ and $\bar{e}$ obtained by the Lŭssi–Greenley method are used (Table 1), the copolymerisation constants calculated from them for VP and butyl vinylsulphonate agree qualitatively and frequently also quantitatively with the experimental values. The values of $\bar{e}$ for VP depend appreciably on the electron-accepting properties of the alkoxy-groups attached to phosphorus and there is a satisfactory linear correlation between the values of $\bar{e}$ and the Taft constants for these groups:

$$\bar{e}=1.75\sigma^*-2.05 \quad (n=5;\ R=0.986;\ s=0.07)\ .$$

This apparently provides an answer to the old question whether or not a relation exists between the capacity of VP for copolymerisation and the nature of the ester residue[37].

In terms of the resonance stabilisation factor Q, which varies from 0.03 to 0.10, VP occupy an intermediate position between typically non-conjugated monomers of the type of ethylene ($Q=0.012$ and VA($Q=0.031$), on the one hand, and conjugated monomers of the type of MA (0.44), AN (0.48), and St (1.0), on the other. For DMVP and DEVP, a linear correlation has been found between $\lg Q$ and the logarithms of the rate constants for the addition of the phenyl radical to the monomers[52]. For DEVP, a similar relation has also been observed between $\lg\bar{Q}$ and the enthalpies of activation for the thermal homolysis of azopropanes $(CH_3)_2C(X)-N=N-(X)C(CH_3)_2$, which are a measure of the energy of stabilisation of the radical by the adjacent substituent X, in the given instance $P(O)(OC_2H_5)_2$.[58] There exist also other similar correlations involving $\lg Q$ or e.[58,59]

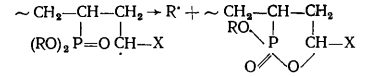
Comparison of the copolymerisation parameters of the structurally related vinyl monomers is extremely instructive (Table 2). It is seen to what extent the data for the organoelemental monomers are similar to one another and differ from those for acrylate. The similarity extends also to the styrene and vinyl acetate systems. In both cases the systems not only belong to the same type ($r_1 < 1$ and $r_2 > 1$ for St; $r_1 < 1$ and $r_2 < 1$ for VA) but are also analogous in form (the values of r_1 and r_2); both monomers have similar reactivities in relation to the macroradicals M_2 ($1/r_2$) and in terms of the alternation parameter r_1r_2. For acrylate, these systems belong to other types ($r_1 < 1$, $r_2 < 1$ and $r_1 > 1$, $r_2 < 1$ respectively) and there are differences between the systems also as regards other parameters. The values of $\bar{Q}$ and $\bar{e}$ for both organoelemental monomers indicate a low degree of conjugation and a high electronegativity. The values of $\bar{Q}$ and $\bar{e}$ for DEVP are lower than for its sulphur analogue, as was to be expected for the transition from the phosphonate to the sulphonate structure, i.e. from a Group V element to a neighbouring Group VI element on the right. The greater electron-accepting capacity of phosphonate and sulphonate compared with acrylate (judging from the values of $\bar{e}$) reflects the greater electronegativity of the metalloids on moving to the right along the Periodic System. (This relation remains valid also for all the VP in Table 1 and for all the acrylates examined by Greenley[26], with the exception of the butyl homologue).

Table 2. Comparison of the copolymerisation parameters of vinyl derivatives of carbon, phosphorus, and sulphur of the type $CH_2=CH-X$ (M_1).

X	M_2 = St				M_2 = VA				$\bar{e}_1$	$\bar{Q}_1$	Refs.
	r_1	r_2	$1/r_2$	r_1r_2	r_1	r_2	$1/r_2$	r_1r_2			
$(C_2H_5O)_2P(O)$	0.06	6.32	0.16	0.38	0.74	0.09	11	0.07	0.92	0.07	[38]
$C_4H_9OS(O)_2$	0.13	2.50	0.40	0.33	0.20	0.04	25	0.01	1.26	0.10	[26,54]
$CH_3OC(O)$	0.18	0.75	1.33	0.14	5.80	0.03	33	0.17	0.60	0.44	[26,51]

The rates of copolymerisation of VP with St, Ma, MMA, and VA decrease with increase of the content of the OPM in the system. On copolymerisation, quadratic termination of kinetic chains, usual for radical polymerisation, takes place[38]. An increase of the content of the OPM in the initial mixture and in the copolymer leads in all cases to a sharp decrease of the intrinsic viscosity and probably of the molecular weight, due to chain transfer to the OPM.[38] The determination of the constants for the chain transfer to the monomer led to the conclusion that the majority of the OPM investigated are chain transfer agents with a moderate activity. In terms of logarithmic coordinates, the constants for the chain transfer of the poly(vinyl acetate) radical to VP are satisfactorily correlated with the constants for the transfer of the same radical to the corresponding compounds of the type of POX_3 in which the vinyl group has been replaced by a third residue $X = OC_2H_5$, OC_3H_7-iso, or $N(CH_3)_2$.[60] However, the chain transfer constants themselves per group X (in the case of the monomers) are greater by 1.5–2 orders of magnitude than for POX_3.

If the chain transfer involves simply the homolytic abstraction of hydrogen, as is frequently stated in the literature[6,21] the above result can be accounted for solely by an increase of the reactivity of the hydrogen atoms in X when a single group X is replaced by a vinyl group, but we do not believe that it is possible to specify unambiguously the cause of such a radical change. Most probably the increased constants for chain transfer to the monomer are associated with the formation of relatively stable conformations of the growing ends of this chain with a greater proximity between the radical centre and the phosphoryl group of the penultimate unit, by analogy with the homopolymerisation of VP.[8,61]. In such a structure there is a possibility of intramolecular substitution leading to the abstraction of R$^\cdot$ which implies the termination of the old molecular chain and the generation of a new one without the termination of the kinetic chain (the so-called non-degradative chain transfer).



R$^\cdot$ + monomers → chain regeneration.

At any rate, there is no doubt about the significant role of the phosphoryl centre in the transfer mechanism.

The copolymerisation of VPA is of great practical interest, because it makes it possible to obtain linear, soluble, phosphorus-containing polyelectrolytes[34,35], despite the low reactivity of the monomer (Table 1).

The copolymerisation of α-PVPA has been studied in detail. In contrast to VPA,[34] this monomer does not undergo homopolymerisation[30], which was explained by the steric hindrance due to the two bulky geminal substituents. However, α-PVPA copolymerises more readily than VPA and its esters, which becomes particularly clear when the relative reactivities with respect to the polystyrene radical are compared (Table 3, the values of $1/r_2$). This is because the radical arising on addition to α-PVPA is stabilised by both substituents— the phenyl and phosphoryl groups. However, the degree of this stabilisation is greatly reduced compared with the monomer having the phenyl substituent alone, which follows directly from the copolymerisation parameters for the α-PVPA–St system[30].

Table 3. Copolymerisation parameters of α-PVPA (M_1).

M_2	t, °C	r_1	r_2	$1/r_2$	Refs	e_1	Q_1
St	70	0.20±0.05	1.50±0.05	0.67	[30]	0.30	0.28
AA	70	0.44±0.03	0.98±0.08	1.02	[63]	1.80	2.86
Acrylamide	80	0.10±0.05	2.55±0.05	0.39	[65]	—	—
AN	70	0.32±0.07	0.69±0.18	1.45	[63]	2.47	3.20
MAA	80	0.36±0.13	3.5±0.2	0.29	[62]	—	—
MMa	80	0.06±0.04	3.3±0.2	0.30	[62]	1.65	0.37
Methacrylamide	80	0	2.28±0.08	0.44	[65]	—	—
Methacrylonitrile	80	0	2.24±0.02	0.45	[64]	—	—
Chloroprene	60	0.10±0.05	7.5±0.1	0.13	[66]	1.05	0.98
2,3-Dichlorobuta-1,3-diene	—	0.07±0.01	7.75±0.10	0.13	[67]	—	—
Divinylbenzene	80	0.05±0.05	1.50±0.01	0.67	[68]	—	—

β-Phenylvinylphosphonic acid, which is isomeric with α-phenylvinylphosphonic acid, and its derivatives, which are 1,2-disubstituted ethylenes, are scarcely capable of copolymerisation and do not form copolymers with MMA and PVA. Nevertheless the constants for the copolymerisation of *trans*-$C_6H_5-CH=CH-P(O)(OC_2H_5)_2$($M_1$) with St have been determined: $r_1 = 0$ and $r_2 = 34 \pm 2$.[69]

Apart from α-PVPA, a study has also been made of the copolymerisation of other α-substituted vinylphosphonates (Table 4). The isopropenyl derivative copolymerises less

effectively than the vinyl derivative. On the other hand, the behaviour of the remaining OPM of this type on the whole occupies an intermediate position between that of the unsubstituted vinylphosphonate and the corresponding acrylates, VA, or vinyl bromide. It is of interest to compare the constants for the copolymerisation of diethyl α-acetoxyvinylphosphonate with both "parent" monomers—DEVP and VA. For the same values of r_1, the constant r_2 is appreciably smaller for VA, which reflects primarily the increase of the resonance stabilisation factor following the introduction of the phosphono-group into VA. The increase of r_2 after the introduction of the phosphono-group into vinyl bromide can be explained analogously. The copolymerisation of α-alkoxycarbonylvinylphosphonates with MMA resembles much more the behaviour of unsubstituted phosphonates than acrylates. In this instance this is a consequence of the enhancement of the electron-accepting properties of the monomer as a result of the introduction of the phosphono-group, which affects both r_1 and r_2 despite the higher values of Q for the OPM considered compared with acrylates.

Table 4. Copolymerisation parameters of the dialkyl esters of α-substituted vinylphosphonic acids $CH_2=C(X)-P(O)(OR)_2$ (M_1).[131]

M_2	t, °C	r_1	r_2	$1/r_2$	e_1	Q_1
		X=CH_3; R=CH_3 *				
St	60	0.23±0.05	8.6±0.6	0.12	—	—
MMA	60	0.2	30	0.03	—	—
VA	60	0.99±0.13	0.14±0.01	7.1	0.58	0.07
		X=$COOCH_3$; R=C_2H_5				
MMA	70	0.2	1.3	0.77	1.54	0.90
		X=$COOC_2H_5$; R=C_2H_5				
MMA	70	0.05±0.05	1.00±0.05	1.0	2.11	1.45
		X=$OCOCH_3$; R=C_2H_5 **				
St	60	0±0.05	3.88±0.37	0.26	—	—
MMA	60	0.01±0.01	4.70±0.60	0.21	1.37	0.23
VA	60	0.60±0.06	0.09±0.02	11.1	0.87	0.06
DEVP	60	0.55±0.20	0.62±0.30	1.61	1.84	0.24
		X=Br; R=C_2H_5				
MMA	70	0.04±0.04	1.25±0.15	0.80	2.11	1.16

Remarks: Copolymerisation parameters and Greenley groups: *$\bar{e}_1=1.12$, $\bar{Q}_1=0.033$ (group V, $n=3$, $R=0.95$); **$\bar{e}_1=0.51$, $\bar{Q}_1=0.076$ (group IV, $n=4$, $R=0.86$).

Vinylphosphines, vinylphosphine oxides, and vinylphosphine sulphides belong to the same type of OPM with the phosphorus atom linked directly to the vinyl group (Table 5). The relative reactivity ($1/r_2$) of diphenylvinylphosphine oxide is greater by a factor of ~3 than that of dialkylvinylphosphine oxide in copolymerisation with both St and MMA and is comparable to the reactivity of the corresponding phosphine. The latter finding is extremely remarkable. It has an analogy in the behaviour of derivatives of tricoordinate and tetra-coordinate sulphur[54,55,71], which also do not differ greatly in reactivity in copolymerisation reactions. In contrast to copolymerisation with St and MMA, where the reactivity of phosphine oxides is much lower than that of the comonomers, in the copolymerisation with VA, as in the case of VP, the reactivity of the OPM is comparable and even somewhat greater than that of VA, which leads to the appearance in the system of products with azeotropic composition.

Divinylphosphinates $(CH_2=CH)_2P(O)(OC_2H_5)$ exhibit a low reactivity in copolymerisation with MMA and St.[72]

III. MONOMERS WITH THE PHOSPHORUS ATOM AT A DIENE GROUP (TYPE B)

This group of monomers includes derivatives of butadienyl- and isopropenylphosphonic acids, butadienylenediphosphonic acids, and the corresponding phosphine oxides.

Table 5. Copolymerisation constants of vinylphosphines, vinylphosphine oxides, and vinylphosphine sulphides of the type $CH_2=CH-X$ (M_1) at 60 °C.[70]

X	M_2	r_1	r_2	$1/r_2$
$(C_6H_5)_2P$	St	0	7±1	0.14
$(C_6H_5)_2P$	MMA	0	5.1±0.2	0.20
$(C_6H_5)_2P(O)$	St	0	5±1	0.20
$(C_6H_5)_2P(O)$	MMA	0	11±4	0.09
$(C_6H_5)_2P(O)$	St	0.4±0.2	12.7±1.2	0.08**
$(C_6H_5)_2P(O)$	VA*	0.49±0.07	0.17±0.01	5.88**
$(iso\text{-}C_4H_9)_2P(O)$	St	0	17±5	0.06
$(iso\text{-}C_4H_9)_2P(O)$	MMA	0	30±10	0.03
$(C_6H_5)_2P(S)$	St	0	2.1±0.3	0.48
$(C_6H_5)_2P(S)$	MMA	0	13±3	0.08

*$e_1=0.74$; $Q_1=0.05$.

**Data of Levin et al.[38]

Table 6. Copolymerisation parameters of monophosphonobutadienes (MPB) of the type $CH_2=CH-C(CH_3)=CHP(O)X_2$ (M_1)

X	M_2	t, °C	r_1	r_2	$1/r_2$	Refs.	e_1	Q_1
Cl	St	75	1.35	0.30	3.30	[73]	0.15	0.47
F	St	75	1.15	0.54	1.90	[74]	−0.11	1.07
F	MMA	80	1.3±0.1	0.20±0.01	5.0	[75]	1.54	5.83
CH_3O	St	75	1.14±0.10	0.40±0.02	2.50	[76]	0.09	1.23
C_2H_5O	VDC	70	2.19±0.40	0.24±0.40	4.17	[77]	1.20	1.49
C_2H_5O	DCVP	70	2.12±0.04	0.15±0.08	6.70	[49]	—	—
C_2H_5O	TEDIP	70	1.22±0.12	0.09±0.01	11.1	[49]	—	—
iso-C_3H_7O	St	75	1.28±0.11	0.67±0.03	1.49	[76]	−0.41	1.09
2,4-$Cl_2C_6H_3O$	isoprene	70	0.04	0.27	3.70	[24]	1.69	3.28
$(C_2H_5)_2N$	VDC	70	0.65±0.05	0.15±0.01	6.67	[77]	1.93	3.20
$(C_2H_5)_2N$	DCVP	70	2.0±0.4	0.10±0.10	10.0	[49]	—	—
$(C_2H_5)_2N$	DEMOP	70	0.23±0.01	0.10±0.10	10.0	[49]	—	—
$(C_2H_5)_2N$	DEIP	70	0.09±0.01	1.22±0.12	0.82	[49]	—	—
$(C_2H_5)_2N$	DEPB	70	0.93±0.04	0.02±0.02	50.0	[49]	—	—
C_2H_5	VDC	70	0.58±0.01	0.08±0.04	12.5	[77]	—	—
C_2H_5	DCVP	70	2.86±0.10	0.06±0.06	16.7	[49]	—	—

Table 6 shows that, in relation to the polystyrene radical, the reactivity ($1/r_2$) of the dichloride and isopropenylphosphonic acid is higher than that of the esters and the reactivity of the latter is much higher than that of the corresponding vinylphosphonates (Table 1) and allylphosphonates (Table 10, see below). The reactivity of diene OPM is higher than that of the vinyl comonomers without phosphorus (St, MMA, and VDC). This makes it possible to obtain copolymers greatly enriched in the OPM. The sharp increase of the reactivity of the OPM of this type in copolymerisation processes is usually caused by the increase of the degree of

conjugation (Q) in the macroradicals formed following addition to the 1,4-dienes. In copolymerisation with isoprene, the products are copolymers with a rigorously alternating structure ($r_1 r_2 = 0.01$).

The study of the copolymerisation of MPB with different structures showed[77] that the reactivity of the OPM in relation to the poly-VDC radical ($1/r_2$) increases in the sequence ester < amide < oxide (Table 6). This is apparently caused by the increase of the values of e for the OPM in view of the electron-accepting nature of the VDC macroradical. An analogous behaviour has been observed also for the carboxy-radicals of the OPM.[78] The activity series established for the OPM varies in opposition to the series based on the rates of homopolymerisation of these monomers[49], i.e. in the given instance the principle of the ideal reactivity of the monomers is maintained[53].

In order to elucidate the relation between the structure and reactivity of phosphonobutadienes in radical copolymerisation with VDC, the correlation between the relative reactivity of the MPB and the electron density at the phosphorus nuclei has been examined[77]; the chemical shift ($\delta_{^{31}P}$) in the ^{31}P NMR spectra and the stretching vibration frequencies of the P=O group in the infrared spectra of the monomers investigated may serve as a measure of this reactivity within fairly narrow reaction series. Linear relations have been observed between these parameters:

$$\lg(1/r_2) = 0.34 - 0.02\,\delta_{^{31}P} \quad (R = 0.997;\ s = 0.028)$$
$$\lg(1/r_2) = 8.5 - 0.006\,\nu_{P=O} \quad (R = 0.999;\ s = 0.033).$$

As might have been expected on the basis of the values of e_1, the reactivity of MPB in relation to the electronegative poly-VDC radical increases with decrease of the stretching vibration frequencies of the phosphoryl group and as the ^{31}P NMR signals are displaced downfield, i.e. with increase of the positive charge on the phosphorus atom.

The determination of the microstructures of the polymers and copolymers by infrared and ^{31}P NMR spectroscopy showed[79] that MPB polymerise mainly in the 3,4-position, because the addition in the 1,4-position and even more so in the 1,2-position is sterically hindered owing to the presence of bulky phosphorus-containing groups. Other 1-substituted dienes with bulky silicon-, germanium-, and tin-containing groups also behave similarly in polymerisation reactions[80-82], while in the radical polymerisation of the less bulky carboxylic acid and ester analogues [$-C(O)OH$, $-C(O)OR$, and $-OC(O)CH_3$] polymers with the predominatly 1,4-structure are formed[78,83-86].

The copolymerisation of 1,3-dienes with two phosphorus atoms is of great interest from the standpoint of the modification of polymeric materials, because this process makes it possible to obtain copolymers with a higher phosphorus content but a lower fraction of OPM units and hence one can achieve the manifestation of the necessary specific properties without a significant alteration of other physicomechanical characteristics of the polymer. For this purpose, a detailed study has been made[49,77,87-89,95,132] of the radical copolymerisation of 2,3-bis[(dialkyl(aryl)]phosphonobutadienes with a whole series of vinyl and diene monomers (Table 7), which permitted a fairly complete estimate of the reactivity of these OPM in relation to different macroradicals.

For the majority of systems (with the exception of MMA, VA, and *N*-vinylpyrrolidinone), both copolymerisation constants are less than unity and $r_1 r_2 \ll 1$, i.e. the comonomers exhibit a considerable tendency towards the formation of copolymers with an alternating structure. The sequence in which the reactivity of the monomers relative to the DEPB radical ($1/r_1$) varies agrees, as for the copolymerisation of DEVP, with the analogous sequence for the majority of radicals free from phosphorus[53]: VA < AN < MMA < VDC < St < isoprene. The relative reactivity of diphosphonobutadienes with respect to the same polymeric radicals ($1/r_2$) is comparable to the reactivity of monophosphonobutadienes (Table 6) and is much higher than the reactivity of other unsaturated OPM. In particular, the reactivity of DEPB with respect to the polystyrene radical is ~20 times higher than the reactivity of DEVP (Table 1).

Table 7. Parameters of the copolymerisation of diphosphonobutadienes of the type $CH_2=C[P(O)(OR)_2]-C[P(O)(OR)_2]=CH_2$ (M_1) with 1-monosubstituted and 1,1-disubstituted ethylenes at 70 °C.

M_2	r_1	r_2	$1/r_1$	$r_1 r_2$	Refs.	e_1	Q_1
			R=C_2H_5*				
Isoprene	0±0.01	0.40±0.05	>100	<0.01	[87]	1.91	1.19
Butadiene	0±0.03	0.42±0.03	>33	<0.01	[87]	0.73	0.50
St	0.06±0.01	0.36±0.07	16.7	0.02	[88]	1.15	0.57
VDC	0.07±0.07	0.22±0.02	14.3	0.02	[77]	2.44	2.67
MMA	0.08±0.05	1.40±0.15	12.5	0,11	[88]	1.86	0.94
4-Vinylpyridine	0.08±0.02	0.40±0.05	12.5	0.03	[132]	1.77	2,22
AN	0.09±0.03	0.43±0.03	11.1	0,04	[132]	3.04	10,40
MVN	0.10±0.06	0.32±0.02	10.0	0.03	[89]	1.50	1,39
2-Vinylpyridine	0.15±0.10	0.60±0.05	6.7	0.09	[89]	1.17	1.22
N-Vinylpyrrolidinone	1.25±0.40	0.02±0.01	0.8	0,02	[132]	0.87	0.83
VA	1.85±0.50	0.05±0.05	0.5	0.09	[132]	0.70	0.17
DCVP	1.00±0.15	0.10±0.05	1.0	0.10	[49]	—	—
DEMOP	0.04±0.04	3.40±0.60	25	0.14	[49]	—	—
TEDIP	0,02±0.02	0.93±0.04	50	0.02	[49]	—	—
			R=C_6H_5				
St	0.11±0.03	0.20±0.08	9.1	0.02	[88]	1.15	1.05
MMA	0.10±0,10	1,40±0.15	10.0	0.14	[88]	1.78	0.92

*$\bar{e}_1 = 1.20$, $\bar{Q}_1 = 0.97$ (group II, $n = 9$, $R = 0.78$).

The study of the copolymerisation of styrene with DPB[88], containing ester groups at the phosphorus atom with different electronegativities, showed that the relative reactivity of DPB with respect to the polystyrene radical is described satisfactorily by the Taft equation

$$\lg(1/r_2) = 0.32\,\sigma^* - 0.08 \quad (R = 0.988;\ s = 0.028).$$

This relation shows that the reactivity of DPB esters is largely determined by the polarity of the alkoxy-groups and is independent of steric effects. The positive sign of the constant ρ^* indicates an increase of the reactivity of the monomers with respect to an electron-donating radical with increase of the electron-accepting properties of the substituents.

The reactivity of DPB with respect to the polystyrene radical is also correlated with the chemical shifts of the signals of the *trans*- and *cis*-terminal protons (in relation to the phosphono-group) in the ^1H NMR spectra and also with the stretching vibration frequencies of the phosphoryl groups of the monomers:

$$\lg(1/r_2) = 1.01\delta_H^{trans} - 6.05\,(R = 0.998;\ s = 0.01)\ ;$$
$$\lg(1/r_2) = 0.76\delta_H^{cis} - 4.33\,(R = 0.982;\ s = 0.03)\ ;$$
$$\lg(1/r_2) = 0.01\,\nu_{P=O} - 12.03 \quad (R = 0.979;\ s = 0.04)\ .$$

The reactivity of DPB increases with increase of the chemical shifts of the protons, i.e. with decrease of the electron density in the diene system and with increase of the stretching vibration frequencies of the phosphoryl groups of the monomers. Using the relations obtained, it is possible to predict with a satisfactory accuracy the relative reactivities of phosphonobutadienes which have not yet been investigated.

Comparison of the behaviour of butadiene and DEPB in radical copolymerisation reactions with a common vinyl comonomer (Table 8) shows that the reactivity of DEPB is appreciably lower than that of butadiene (lower values of r_1). In all systems an inversion of the reactivities of the monomers can be observed, i.e. the diene becomes less reactive than the comonomer. The introduction of two phospheno-groups into the butadiene molecule reduces the reactivity of the diene system, which is caused, among other factors, by the steric hindrance due to the phosphonate groups. In terms of the relative reactivity ($1/r_2$) with respect to the macroradicals of the electron-donating type (St. MVP), DEPB is more reactive than butadiene, while with respect to electron-accepting radicals (MMA, VDC, AN), butadiene is actually more reactive than DEPB, which can be accounted for by the difference between the electronic natures of these diene monomers ($\bar{e}_{\text{butadiene}} = -1.36$; $\bar{e}_{\text{DEPB}} = 1.20$).

Table 8. Comparison of the copolymerisation constants of butadiene and DEPB.

M_2	DEPB (M_1) (Refs.88,132)		Butadiene (M_1) (Refs.51,90)	
	r_1	r_2	r_1	r_2
St	0.06	0.36	1.35	0.58
MMA	0.08	1.40	0.62	0.18
VDC	0.07	0.22	1.90	0.05
AN	0.09	0.43	0.33	0.25
MVP	0.10	0.32	1.32	0.72

From the values of $\bar{e}$ and $\bar{Q}$, DPB must be regarded as electron-accepting highly conjugated monomers. The high specific reactivities of DPB can be accounted for by the presence of the conjugated 1,3-diene system in these compounds, which ensures the effective resonance stabilisation of the resulting radicals, while the high positive values of the polarity factors are due to the presence of two electronegative phosphonate groups in the monomers. Naturally the values of $\bar{e}$ and $\bar{Q}$ for DPB are much higher than the corresponding values for monovinyl OPM. The higher reactivity of diene derivatives in copolymerisation compared with the vinyl derivatives is due largely to the higher values of Q.

Analysis of the infrared and ^{31}P NMR spectra of the monomers and polymers has shown[77,79] that, in contrast to MPB, the polymerisation of DPB proceeds preferentially in the 1,4-position. The rate of copolymerisation of DPB is proportional to the concentration of the monomers and the square root of the initiator concentration, which indicates the bimolecular termination of the polymer chains and the absence of degradative chain transfer[87,91]. In this respect phosphonobutadienes do not differ from VP.[38]

Significant differences have been observed in the study of the dependence of the rate of polymerisation and the molecular weight of the copolymers on the composition of the initial monomer mixture[25,77,87-89,91]. In the copolymerisation of DPB with MMA, AN, VDC, and certain other monomers the rate of reaction diminishes with increase of the OPM content in the initial mixture (as for VP), which is apparently caused by the replacement of the active polymeric radical derived from the vinyl monomer by the less active phosphorus-containing radical of the allyl type stabilised by conjugation. The molecular weight (intrinsic viscosity) of the copolymer also diminishes under these conditions but less markedly than the yield of the copolymer, which nevertheless makes it possible to obain high-molecular-weight polymers with a fairly high phosphorus content.

The constants for chain transfer by the poly-MMA radical to DEPB, 2,3-bis(diphenylphosphono)buta-1,3-diene, and 2,5-dimethyl-3,4-bis(diethylphosphono)hexa-2,4-diene have been determined[88] from the Mayo equation[92]. Virtually identical chain transfer constants were obtained for all three DPB, amounting to $(2.9-3.3) \times 10^{-3}$, whence it follows that the chain transfer constants depend little or not at all on the nature of the alkoxy-groups. Consequently the chain transfer reaction is not associated with the abstraction of a hydrogen atom from these groups, as for vinyl OPM,[38] since otherwise the phenyl ester would have shown a much smaller reactivity than the ethyl ester. The methyl groups in 2,5-dimethyl-3,4-bis(diethylphosphono)-hexa-2,4-diene are also not significantly involved in the chain transfer reaction, since their presence in this diene does not increase the chain transfer constant[93]. In terms of the absolute values of the chain transfer constants in the polymerisation of MMA, DPB can be characterised as chain transfer agents of moderate activity, but they are much more active than the MMA comonomer [$(0.7-1.8) \times 10^{-5}$ at 60 °C].[94]

Other features are observed in the copolymerisation of DPB with isoprene, St, vinylpyridines, and MAn, i.e. with strong electron-donating and electron-accepting conjugated monomers. In this case the dependence of the yield and the molecular weight of the copolymers on the composition of the initial monomer mixture passes through an extremum. An extremum in the yield and moleclar weight of the copolymers is observed also in many instances for MPB, particularly in the copolymerisation of bis-2,4-dichlorophenyl 2-methylbuta-1,3-dienylphosphonate with isoprene[24].

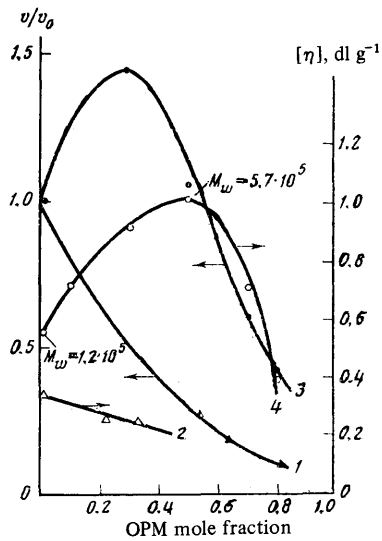
Thus organophosphorus polymers with a higher molecular weight than the corresponding purely organic homopolymers can be obtained by the copolymerisation of diene OPM with many comonomers, which constitutes an important advantage of OPM over VP in the copolymerisation of which the rate of reaction and the molecular weight of the polymers are much lower, as mentioned above. The advantages of diene OPM are clearly illustrated in the Figure, which presents the dependence of the relative rates of the process and of the molecular weight (intrinsic viscosity) of the copolymers in the copolymerisation of DEPB and DEVP with St on the composition of the initial monomer mixtures.

The tendency of phosphonobutadienes to form copolymers with an alternating structure and the extrema in the dependence of the rates of copolymerisation and the molecular weights of the copolymers on the composition of the monomer mixture may indicate[95] the formation by these OPM of charge-transfer complexes (CTC) with the comonomer.

The formation of the 1:2 CTC in the DEPB–MAn system has been demonstrated by ^1H NMR and ultraviolet spectroscopy[96]. In the copolymerisation in this system a high degree of regularity in the alternation of monomer units in the copolymer and maxima in the rate and the molecular weight of the copolymers have been observed.

The copolymerisation of DEPB with MAn in the presence of any amount of acetone, tetrahydrofuran, and acetonitrile leads to the formation of a copolymer which does not differ in composition from the polymer obtained in the absence of

these additives; however, the introduction of dimethylformamide (DMF), dimethyl sulphoxide (DMSO), and particularly dimethylaniline into the system increases the reactivity of MAn. In terms of their influence on the reactivity of MAn, these compounds can be arranged in the sequence: DMF < DMSO ≪ dimethylaniline. This sequence is apparently caused by the decrease in the same series of the ionisation potentials of the compounds. The absence of an influence on the course of copolymerisation by other electron donors can evidently be accounted for by their inability to compete with DEPB in the donor–acceptor interaction with MAn.[96]



Dependence of the relative rates of copolymerisation v/v_0 (curves *1* and *3*) and the intrinsic viscosities of the copolymers [η] (curves *2* and *4*) on the composition of the monomer mixture in the copolymerisation of OPM with St; OPM: *1*) and *2*) DEVP; *3*) and *4*) DEPB.

With increase of the DMF concentration, r_2 increases sharply, while r_1 decreases[96,97], which indicates an appreciable increase of the reactivity of MAn in the presence of DMF. Thus the composition of the copolymers can be regulated within very wide limits by introducing electron-donating compounds into the system.

Data on the copolymerisation of DEPB with various imides of maleic acid have been published[98]. In these systems the reactivity of the monomers is independent of both the nature (DMF, dioxan) and the amount of the solvent employed. The relative reactivity of *N*-alkylmaleimides in relation to the DEPB macroradical ($1/r_1$) obeys the Taft equation:

$$\lg(1/r_1) = 0.80\,\sigma^* + 0.47 \quad (R = 0.999;\ s = 0.004)\ .$$

For *N*-arylmaleimides, a relation has been observed between the reactivity and the inductive constants σ_I of the substituents in the aryl residue:

$$\lg(1/r_1) = 0.46\,\sigma_I + 1.3 \quad (R = 0.990;\ s = 0.022)\ .$$

A study of the copolymerisation of allene OPM–diethyl and dibutyl 3-methylbuta-1,2-dienylphosphonates—with MA (M_2) established[99] that the allene derivatives of phosphorus are characterised by a low reactivity ($r_1 = 0$, $r_2 \gg 1$).[99] The replacement of the diene group by the allene group reduces sharply the copolymerisation capacity of the OPM, which was in fact to be expected in view of the absence of conjugation in the π-electron system of the allene group.

IV. MONOMERS WITH THE PHOSPHORUS ATOM IN THE β- OR γ-POSITION RELATIVE TO A VINYL GROUP (TYPE C)

Vinyl and allyl phosphates and vinyl- and allyl-phosphonates should be included in this group of monomers. It follows from Table 9 that vinyl phosphates copolymerise much more readily with structurally analogous vinyl esters than with St. The reactivity of vinyl phosphates in copolymerisation with St is very low and in practice only the St homopolymer is formed. The relative reactivity of vinyl phosphates in reactions with macroradicals is much lower, as was to be expected (by analogy with carboxy-analogues), than the reactivity of VP and is comparable to the reactivity of VA. The quantities Q and $\bar{Q}$ are on the whole lower than for VP, i.e. the introduction of oxygen between the vinyl group and phosphorus reduces the conjugation between the vinyl group and the phosphorus-containing residue which was in any case already low. This is also evident from the behaviour of diethylvinyl phosphate in relation to C_6H_5.[52] The copolymerisation with MAn likewise resembles the behaviour of VA and is characterised by a high degree of regularity in the alternation of units.

Table 9. Copolymerisation parameters of vinyl phosphates of the type $CH_2=CH-O-P(O)(OR)_2$ (M_1) at 60 °C.

M_2	r_1	r_2	$1/r_2$	Refs.	e_1	Q_1
			R=CH_3			
St	0±0.1	23.0±5.0	0.04	[38]	—	—
VA	0.19±0.04	1.28±0.06	0.78	[38]	−2.03	0.01
			R=C_2H_5 *			
St	0.04±0.10	91±30	0.01	[38]	—	—
VA	0.25±0.09	1.59±0.10	0.63	[38]	−1.80	0.04
Vinyl chloroacetate	0.43	2.0	0.50	[100]	−1.04	0.07
VC	0.20	3.3	0.30	[100]	−0.44	0.02
MAn	0	0.2	5.0	[100]	—	—
			R=C_6H_5			
Vinyl chloroacetate	0.50	1.4	0.71	[100]	−0.83	0.02
VC	0.25	2.8	0.36	[100]	−0.40	0.02
MAn	0	0.2	5.0	[100]	—	—

*$\bar{e}_1 = -3.04$, $\bar{Q}_1 = 0.06$ (group IV, $n = 4$, $R = 0.84$).

There have been many communications on the copolymerisation of allyl derivatives of phosphorus[5,101], but the majority of the investigators restricted themselves to the determination of the phosphorus content in the copolymers and to estimating some of their properties. The available quantitative data on the compolymerisation of monoallyl derivatives of phosphorus are presented in Table 10. In terms of their ability to react with the poly-MAA radical, the monomers listed in Table 10 can be arranged in the sequence DEVP > diethyl allylphosphonate > 1,4-bis(diethylphosphono)-but-2-ene[102]. This sequence in the variation of the reactivities

is associated with the decrease of Q on passing from the vinyl to the allyl monomer (rupture of the conjugation chain) and with the transition from the mono- to the 1,2-disubstituted ethylene; the latter always causes a sharp reduction in the reactivity of monomers. Allyl derivatives of phosphorus exhibit a lower reactivity in copolymerisation with unsaturated polyesters[104,105].

Table 10. Parameters of the copolymerisation of allyl derivatives of phosphorus.

M_1	M_2	t, °C	r_1	r_2	$1/r_2$	Refs.	e_1	Q_1
$CH_2=CHCH_2P(O)(OCH_3)_2$	AN	—	0.05±0.02	4.70±0.18	0.21	[39]	2.44	0.45
$CH_2=CHCH_2P(O)(OC_2H_5)_2$	MAA	60	0.04±0.04	6.1±0.4	0.17	[102]	1.79	0.15
$CH_2=CHCH_2P(O)(OC_2H_5)_2$	DMA	80	0.07	52.5	0.02	[103]	—	—
$CH_2=CHCH_2P(O)(OC_2H_5)_2$	AN	—	0	4.30±0.18	0.23	[39]	—	—
$CH_2=CHCH_2P(O)(OC_2H_5)_2$	PBGF*	80	0.12±0.08	9.25±3.00	0.11	[104]	—	—
$CH_2=CHP(O)(OC_2H_5)_2$	MAA	60	0.15±0.15	1.9±0.5	0.53	[102]	1.72	0.45
$CH_2-CH=CH-CH_2$ $P(O)(OC_2H_5)_2$ $P(O)(OC_2H_5)_2$	MAA	60	0±0.10	12.0±1.0	0.08	[102]	—	—
$CH_2=CHCH_2OP(H)(=O)OC_2H_5$	PBGF	80	0.03±0.03	5.5±2.5	0.18	[105]	—	—

*PBGF = poly(1,3-butylene glycol fumarate).

Table 11. Copolymerisation constants of diallyl OPM.

M_1	M_2	t, °C	r_1	r_2	$1/r_2$	Refs.
$(CH_2=CHCH_2O)_2P(O)C_6H_5$	DMA	80	0.09	18.7	0.05	[103]
$(CH_2=CHCH_2O)_2P(O)C_6H_5$	DMA	80	0.07	19.5	0.05	[103]
$(CH_2=CHCH_2O)_2P(O)C_6H_5$	MMA	70	0.14	22.96	0.04	[106]
$(CH_2=CHCH_2O)_2P(O)C_6H_5$	St	70	0.03	28.97	0.03	[106]
$(CH_2=CHCH_2O)_2P(O)(OC_6H_4)$	MMA	70	0.22	9.78	0.10	[107]
$(CH_2=CHCH_2O)_2P(O)(OC_6H_4)$	St	70	0.15	16.84	0.06	[107]
$[(CH_2=CHCH_2O)_2P=N]_3$	St	70	0.22	0.51	1.96	[108]
$(CH_2=CHCH_2)_2P(O)C_6H_5$	DMA	80	−0.01±0.01	18.1±0.4	0.06	[109]
$(CH_2=CHCH_2)_2P(O)C_6H_5$	DMA	110	−0.01±0.02	11.1±0.4	0.09	[109]
$(CH_2=CHCH_2)_2P(O)C_6H_5$	DMA	140	−0.09±0.02	5.59±0.24	0.18	[109]

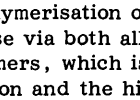
A number of studies[103,106–109] have been devoted to the copolymerisation of diallyl OPM (Table 11), which copolymerise via both allyl groups with formation of cyclolinear polymers, which is indicated by the lower degree of unsaturation and the high solubility of the products. Table 11 shows that phosphonates are relatively inactive monomers. The relative reactivities of butyl- and phenyl-phosphonates are the same, i.e. the presence of acid groups does not influence the reactivity of the monomers which is apparently due to the remoteness of these groups from the double bond. On passing to the phosphates, the reactivity of the OPM increases somewhat. The reactivity of diallyl derivatives of phosphorus with respect to the polymeric methacrylate radicals is approximately the same regardless of their structure and somewhat higher than the reactivity of allyl OPM (Table 10). With increase of temperature, the reactivity of the OPM with respect to the poly-DMA radical increases. It is believed[109] that the negative values of r_1 are due to the influence of the penultimate unit but one cannot rule out the possibility that other factors also operated, since the experiments were performed at fairly high temperatures where there is a possibility of depolymerisation and of other processes.

The copolymerisation of diallyl methylphosphonate with ethylene[110], in contrast to the copolymerisation with MMA and St, involves one of the allyl bonds. Since the copolymerisation was carried out[110] at low OPM concentrations, only the constant r_2 can be determined with an adequate accuracy. It decreases with increasing pressure, while r_1 is stated by the author to lie in the range between 0 and 2.

V. MONOMERS WITH THE PHOSPHORUS ATOM REMOTE FROM A VINYL GROUP (TYPE D)

This class of OPM includes mainly substituted acrylates, methacrylates, and styrene derivatives. They copolymerise almost in the same way as the analogous monomers without phosphorus. Data on the copolymerisation of phosphonoacrylates with vinyl monomers are presented in Table 12, from which it follows that phosphonoacrylates enter into the composition of the copolymer with somewhat more difficulty than MA and MMA, while in the copolymerisation with St their reactivities are comparable, i.e. the copolymerisation resembles that in the MMA–St system. Naturally the ability of phosphonoacrylates to combine with macroradicals is much greater than that of VP, which makes it possible to obtain polymers with a high phosphorus content. The factors Q and e for phosphonoalkyl methacrylates are frequently close to the corresponding parameters for MMA.

Table 12. Copolymerisation parameters of methacryloyl derivatives of phosphorus $CH_2=C(CH_3)COOR$ (M_1).

R	M_2	t, °C	r_1	r_2	Refs.	e_1	Q_1
$(C_6H_5O)_2P$	St	60	0.09±0.01	2.08±0.01	[111]	0.49	0.17
$(C_6H_5O)_2P$	MMA	60	0.05±0.01	3.97±0.01	[111]	—	—
$(C_6H_5O)_2P(O)$	St	60	0.01±0.01	0.32±0.01	[111]	1.60	0.46
$(C_6H_5O)_2P(O)$	MMA	60	0.11±0.01	0.70±0.01	[111]	—	—
$(BrCH_2CH_2O)(C_6H_5O)P(O)$	AN	40	2.20	0.27	[113]	1.96	4.34
$(C_6H_5O)_2P(O)CH_3$ *	MA	75	0.29±0.05	0.88±0.09	[114]	1.77	1.01
$(C_6H_5O)_2P(O)CH_3$ *	MMA	75	0.27±0.01	1.88±0.03	[114]	1.20	0.55
$(C_6H_5O)_2P(O)CH(CH)_3$ *	MMA	65	0.15±0.03	2.02±0.05	[114]	1.47	0.56
$(C_6H_5O)_2P(O)CH_3$	MMA	68	0.50±0.03	1.43±0.05	[114]	0.96	0.65
$(C_6H_5O)_2P(O)CH_3$	VDC	70	1.50±0.15	0.40±0.06	[132]	1.12	0.87
$(C_6H_5O)_2P(O)CH_3$	DCVP	70	1.35±0.22	0.15±0.09	[49]	—	—
$(C_6H_5O)_2P(O)CH_3$	GEDIP	70	0.10±0.01	0.23±0.01	[49]	—	—
$(C_6H_5O)_2P(O)CH_3$	DEPB	70	3.40±0.60	0.04±0.04	[49]	—	—
$(CH_3O)_2P(O)CH_2CH_3$	St	80	0.49±0.03	0.37±0.02	[115]	0.51	0.95
$(C_2H_5O)_2P(O)CH_2CH_3$	St	80	0.45±0.02	0.39±0.02	[115]	0.52	0.89
$(C_4H_9O)_2P(O)CH_2CH_3$	St	80	0.35±0.01	0.46±0.02	[115]	0.55	0.74
 $P(O)CH_2CH_3$	St	80	0.55±0.02	0.34±0.01	[115]	0.49	1.04
$(C_6H_5)_2P(S)OCH_2CH_3$	St	70	0.38	0.47	[116]	0.51	0.73
$(C_6H_5)_2P(S)OCH_2CH_3$	MMA	70	0.45	0.88	[116]	1.35	1.24
$(CH_3)(C_6H_5O)P(O)OCH_2CH_3$	St	70	0.31	0.50	[117]	0.56	0.67
$(CH_3)(C_6H_5O)P(O)OCH_2CH_3$	MMA	70	0.43	0.49	[117]	1.63	2.46
$(CH_3)(C_6H_5O)P(O)OCH_2CH(Cl)$	St	70	0.07±0.01	2.00±0.05	[117]	0.60	0.16
$(CH_3)(C_6H_5O)P(O)OCH_2CH(Cl)$	MMA	70	0.01±0.01	1.51±0.05	[118]	2.43	1.08
$(CH_3)(C_6H_5O)P(O)OCH_2CH(Cl)$	St	70	0.14±0.01	1.10±0.05	[119]	0.57	0.30
$(CH_3)(C_6H_5O)P(O)OCH_2CH(Cl)CH_2$	St	70	0.12±0.01	3.36±0.05	[118]	0.15	0.14
$(CH_3)(C_6H_5O)P(O)OCH_2CH(Cl)CH_2$	MMA	70	0.30±0.02	1.61±0.05	[118]	1.23	0.64
$(CH_3)(C_6H_5O)P(O)OCH_2CH(Cl)CH_2$	MMA	70	0.45±0.05	0.86±0.05	[119]	1.35	1.26
$(CH_3)(C_6H_5O)P(O)OCH_2CH(Cl)CH_3$	VDC	70	0.14±0.01	0.85±0.05	[119]	1.85	0.54
$(CH_3)(C_6H_5O)P(O)OCH_2CH(Cl)CH_3$	butyl acrylate	70	0.27±0.01	0.97±0.05	[119]	1.90	0.73
$(C_6H_5)(C_6H_5O)P(O)OCH_2CH(Cl)CH_3$	St	70	0.39±0.01	1.87±0.05	[118]	0.24	0.34
$(C_6H_5)(C_6H_5O)P(O)OCH_2CH(Cl)CH_3$	MMA	70	0.26±0.02	1.37±0.05	[118]	1.40	0.81
$(CH_3)(C_6H_5O)P(O)OCH_2CH(OH)CH_2$	St	70	0.04±0.01	1.99±0.10	[119]	0.79	0.14
$(C_6H_5O)_2P(O)OCH_2CH(Cl)CH_2$	St	60	0.37±0.01	0.64±0.08	[120]	0.40	0.60
$(C_6H_5O)_2P(O)OCH_2CH(Cl)CH_3$	MMA	60	0.73±0.03	1.20±0.13	[120]	0.74	0.72
$(C_6H_5O)_2P(O)OCH_2CH(Cl)CH_3$	St	60	0.22±0.03	0.47±0.02	[120]	0.71	0.64
$(C_6H_5O)_2P(O)OCH_2CH(Cl)CH_3$	MMA	60	0.57±0.01	0.81±0.01	[120]	1.26	1.30
$(C_6H_5O)_2P(O)OCH_2CH(Cl)CH_3$	St	60	0.65±0.04	0.22±0.04	[120]	0.60	1.50
$(C_6H_5O)_2P(O)OCH_2CH(Cl)CH_3$	MMA	60	0.33±0.03	0.76±0.05	[120]	1.56	1.55

*Acryloyl derivatives.

Examination of data for the copolymerisation of phosphonoalkyl methacrylates with St (Table 12) shows that the nature of the phosphorus-containing group nevertheless does exert some influence on the reactivity of these monomers, but the nature of this influence is not clear. We can only note that the higher electronegativity of the diphenyl phosphate group compared with the phosphite group also leads to a greater reactivity of methacryloyl phosphate also in relation to the polystyrene radical, compared with methacryloyl phosphite[111]. At the same time vinylphosphines and *p*-styrylphosphines have virtually the same copolymerisation constants as their oxides. This behaviour of the methacryloyl derivatives in cases where the influence of the environment of the phosphorus should be manifested to an even lesser extent requires further experimental confirmation particularly since methacryloyl phosphates are thermally unstable[112]

Styrenes with phosphorus-containing groups in the ring belong to monomers of the same type. The copolymerisation of the chloride and the dibutyl ester of *p*-styrylphosphonic acid with certain monomers has been investigated[121]. On the basis of the available data for the compositions of the copolymers and the initial mixtures, one may conclude that the ester is much more reactive than VA in copolymerisation while the acid chloride has a reactivity comparable to those of St and MMA.

The study of the copolymerisation of the styrenes listed in Table 13 [122,123] showed that these monomers are more reactive than St and MMA and that $r_1 > 1$ and $r_2 < 1$. This makes it possible to obtain copolymers greatly enriched in the OPM over the entire range of initial compositions. It is of interest that Q increases following the introduction of phosphorus-containing groups in St, evidently as a result of their inclusion in the conjugation chain. The quantity e also naturally increases as a result of the introduction of electronegative phosphorus-containing groups. It follows from Table 13 that the relative reactivities of both phosphine (P^{III}) and phosphine oxide and sulphide (P^{IV}) are virtually the same. The similar influence of groups with P^{III} and P^{IV} on the reactivity of the double bond in OPM of type A was noted above but, as already stated, the situation is different for methacrylates.

Table 13. Copolymerisation parameters of diphenyl-*p*-styrylphosphine, its oxide, and its sulphide of the type $CH_2=CH-C_6H_4-X$ (M_1). [123]

X	M_2	t, °C	r_1	r_2	$1/r_2$	e_1	Q_1
$(C_6H_5)_2P$ *	St	65	1.11±0.12	0.46±0.07	2.17	+0.02	1.13
$(C_6H_5)_2P$	St	60	1.43±0.25	0.52±0.05	1.92	−0.30	1.25
$(C_6H_5)_2P$	MMA	60	0.91±0.12	0.32±0.02	3.13	−0.73	1.54
$(C_6H_5)_2P(O)$	St	60	1.40±0.15	0.42±0.02	2.38	−0.07	1.34
$(C_6H_5)_2P(O)$	MMA	60	1.46±0.10	0.38±0.02	2.63	−0.39	1.47
$(C_6H_5)_2P(S)$	St	60	1.49±0.33	0.43±0.05	2.33	−0.13	1.37
$(C_6H_5)_2P(S)$	MMA	60	1.22±0.34	0.29±0.01	3.45	−0.64	1.76

*According to the data of Braun et al. [122]

The data presented in Table 13 on the copolymerisation of styrenes substituted with phosphorus-containing groups in the *p*-position are described satisfactorily by the familiar[124,125] linear relation between the relative reactivity of the styrene monomers with respect to the polystyrene radical and the Hammett constants. The σ constants of the substituents taken from Tsvekov and coworkers[126,127] were used:

$$\lg(1/r_1) = 0.57\sigma + 0.14 \quad ,$$

i.e. phosphorus-containing styrenes obey the same relations as other *p*-substituted styrenes.

The styrene derivatives of arsenic, antimony, and bismuth with structures analogous to that of diphenyl-*p*-styrylphosphine exhibit the same reactivity as the phosphine in copolymerisation with St. [122]

VI. COPOLYMERISATION OF ORGANOPHOSPHORUS MONOMERS OF DIFFERENT TYPES

Direct comparison of the reactivities of different types of OPM in their copolymerisation with one another is of interest[49]. (see Tables 1, 6, and 12). Table 1 shows that acrylic and diene OPM have much higher reactivities than VP.

In the copolymerisation of diene OPM the ester of isoprenylphosphonic acid is more reactive than the amide (Table 6), as has been observed also for acrylic acid derivatives[128], and MPB are more reactive than DPB (Table 6). Phosphonoalkyl methacrylates have an activity comparable to that of monophosphonobutadienes, but higher than that of diphosphonobutadienes (Table 12). The reactivity of MPB with respect to the electronegative DCVP macroradical (Table 6) increases, like that with respect to the poly-VDC radical[77], with decrease of the stretching vibration frequencies of the phosphoryl group and with increase of the negative chemical shifts $\delta_{^{31}P}$:

$$\lg(1/r_2) = 0.59 - 0.02\,\delta_{^{31}P} \quad (R = 0.995;\ s = 0.028)$$

$$\lg(1/r_2) = 7.1 - 0.005\,\nu_{P=O} \quad (R = 0.993;\ s = 0.033).$$

The reactivity of phosphonoalkyl methacrylate with respect to the poly-DCVP radical ($1/r_2$) is comparable to that of isoprenylphosphonate but somewhat lower than the reactivity of butadienylenediphosphonate (Table 1), in agreement with data for the copolymerisation of these monomers with St[76,88,115].

Table 14. The relative reactivities ($1/r_2$) of organophosphorus monomers (M_1) with respect to the polystyrene radical.

OPM	$1/r_2$	Refs.
$CH_2=CH-C(CH_3)=CHP(O)Cl_2$	3.33	[73]
$CH_2=C[P(O)(OC_2H_5)_2]-C[P(O)(OC_2H_5)_2]=CH_2$	2.80	[88]
$CH_2=C(CH_3)C(O)OCH_2CH_2P(O)(OC_2H_5)_2$	2.56	[115]
$CH_2=CH-C(CH_3)=CHP(O)(OCH_3)_2$	2.50	76]
$CH_2=CH-C_6H_4-P(O)(C_6H_5)_2$	2.38	[123]
$CH_2=CH-C_6H_4-P(S)(C_6H_5)_2$	2.33	[123]
$CH_2=C(CH_3)C(O)OCH_2CH_2OP(S)(C_6H_5)_2$	2.14	[116]
$CH_2=CH-C_6H_4-P(C_6H_5)_2$	1.92	[123]
$CH_2=C(CH_3)C(O)OCH_2CHCH_2OP(O)(OC_2H_5)_2$	1.56	[120]
$CH_2=C(C_6H_5)-P(O)(OH)_2$	0.67	[30]
$CH_2=CH-P(O)(OC_6H_5)_2$	0.49	[37]
$CH_2=CH-P(O)(C_6H_5)_2$	0.20	[70]
$CH_2=CH-P(O)(OC_2H_5)_2$	0.16	[38]
$CH_2=CH-P(O)[N(CH_3)_2]_2$	0.16	[38]
$CH_2=CH-P(C_6H_5)_2$	0.14	[70]
$(CH_2=CHCH_2O)_2P(O)(OC_6H_5)$	0.06	[107]
$CH_2=CH-P(O)(OH)_2$	0.04	[34]
$(CH_2=CHCH_2O)_2P(O)(C_6H_5)$	0.03	[106]
$CH_2=CHOP(O)(OC_2H_5)_2$	0.01	[38]

VII. CONCLUSION

It is of interest to examine the reactivities of OPM of different types and with different structures in relation to the standard polystyrene radical (Table 14). Evidently the reactivity of OPM varies within very wide limits: the reactivities of the first and last OPM differ by more than two orders of magnitude. This reactivity series is apparently on the whole analogous to the series for other polymeric radicals, as can be seen from Table 15, which presents the reactivities of the most thoroughly investigated OPM with respect to various macroradicals. The behaviour of new OPM can be assessed and the most promising of these can be selected on the basis of similar series.

Table 15. The relative reactivities ($1/r_2$) of OPM (M_1) in reactions with various polymeric radicals

OPM	St [38, 76, 88, 115]	MMA [45, 88, 114]	VDC [77, 132]	VA [38, 132]	VC [47]
$CH_2=C[P(O)(OC_2H_5)_2]-C[P(O)(OC_2H_5)_2]=CH_2$	2.80	0.71	4.55	20.0	—
$CH_2=CH-C(CH_3)=CHP(O)(OR)_2$	2.50*	—	4.17**	—	—
$CH_2=C(CH_3)-C(O)O-(CH_2)_n-P(O)(OC_2H_5)_2$	2.56***	0.70****	2.50****	—	—
$CH_2=CHP(O)(OCH_2CH_2Cl)_2$	0.41	0.03	0.49	25.0	1.92

* $R = CH_3$. ** $R = C_2H_5$. *** $n = 2$. **** $n = 1$.

Tables 14 and 15 show that diene, methacrylate, and styrene derivatives of phosphorus are most suitable for the modification of polymers by the copolymerisation method. However, the synthesis of the last two types of monomers is extremely laborious, the latter being obtained in low yields and frequently with a low purity. Furthermore, the presence of bulky side groups in the chain at the phosphorus atom greatly reduces the thermal stability of copolymers based on them[129,130].

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As can be seen from the foregoing, the method of the copolymerisation of unsaturated OPM can be used successfully to modify a wide variety of polymeric materials. By altering the nature and the structure of OPM, it is possible to vary widely both the rate of the process and the molecular weights of the products, on the one hand, and the composition of the copolymers and ultimately the properties of the polymers in the desired manner, on the other.

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The Adsorption - Absorption Gas Chromatography on Silochromes with Layers of Liquid Crystals

Z.P.Vetrova, N.T.Karabanov, G.G.Maidachenko, and Ya.I.Yashin

The results of studies of the properties of liquid crystals in a version of gas adsorption-absorption chromatography are surveyed. A general property of liquid crystals deposited on active adsorbent carriers, consisting in the possibility of extending the temperature range of the existence of their mesomorphic state, is revealed.
The bibliography includes 94 references.

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I. INTRODUCTION

Liquid crystals (LC) possess simultaneously the properties of liquids (fluidity, the ability to exist in the form of drops, etc.) and the properties of solid crystalline bodies (anisotropy, and electrical, optical, and other properties)[1]. Friedel[2] was the first to introduce the concept of the mesomorphic (liquid crystal) state and divided liquid crystals into two types: nematic and smectic. Certain liquid crystals belong to both types. In this case the smectic mesophase, in which molecules are not only arranged parallel to one another but are also fixed in layers, is formed initially; at higher temperatures there is a transition to the nematic mesophase, where this additional order is lost. A further increase of temperature leads to the formation of the isotropic liquid. The formation of a special kind of "twisted structure" is characteristic of the cholesteric mesophase, which is regarded as a variety of the nematic phase[1].

Liquid crystals can be formed not only on fusion of a solid (thermotropic liquid crystals) but also in the course of its dissolution (lyotropic liquid crystals). The chemical features, structure, and properties of low-molecular-weight liquid crystals have been described in reviews[3-5] and in a monograph[6].

The liquid crystal state is characteristic not only of many low-molecular-weight compounds but also of high-molecular-weight compounds. As early as 1941, Kargin and Slonimskii[7] and later Sanderman and Keller[8] drew attention to the possibility of the existence of the liquid crystal state in polymeric systems. However, theoretical and experimental studies only recently established that the phase transition of polymers to the mesomorphic state is just as feasible as for low-molecular-weight compounds.

The formation of liquid crystal polymers induced by the entropy effect as a result of the rigidity of the main chain has been described in a review[9]. Liquid crystal systems in which the ordering of the side groups is possible by virtue of the flexibility and not rigidity of the main chain have been examined, for example, in Refs.10–13. Plate et al.[14] proposed a new approach to the formation of liquid crystals of the thermotropic type from high-molecular-weight, which consists in synthesising mushroom-shaped polymers containing mesogenic groups at the ends of the side branches. The mesomorphic state of liquid crystals possesses a unique combination of properties, which is responsible for their wide scale employment in optics, holography, quantum electronics, visual observations of temperature changes by only 0.01–0.001 K, and the elucidation of molecular structures by NMR spectroscopy, as structural elements in living organisms, and finally as specific sorbents in the chromatographic separation of isomeric compounds. The applications of liquid crystals have been reviewed fairly completely[15].

On the other hand, the first studies of the chromatographic characteristics of liquid crystals demonstrated their likely usefulness as sorbents for gas chromatography[16-19]. The ordered arrangement of molecules in the temperature range of the mesophase promotes the separation of aromatic *meta*- and *para*-isomers with similar boiling points. This effect, first observed[16-19] for azoxy-esters, proved to be characteristic of many liquid crystals: it arises because the more linear form of the *para*-substituted aromatic compounds enables them to penetrate more readily into the liquid crystal lattice and to interact more "intimately" than the *meta*- and *ortho*-substituted derivatives. This property has been noted in a number of studies[20-27] where it was shown that the maximum selectivity of the liquid crystals with respect to positional isomers is observed at the melting point and diminishes with increase of temperature, while the sorption capacity of the chromatographic column also increases sharply on passing from solid to the mesomorphic state of the liquid crystal.

Liquid crystals have found extensive applications in gas chromatography as highly selective stationary phases. Fairly numerous publications, including reviews, have been devoted to this problem[22,23,28-30]. The possible analytical applications of many known and also newly synthesised liquid crystals have been investigated by Soviet workers[28,31-42]. Difficult separations have been achieved on liquid crystals using not only packed but also micropacked[43] and capillary columns[44-47]. Chemical modification of the silica surface with cholesteric liquid crystals makes it possible to employ such sorbents for highly effective liquid chromatography[48].

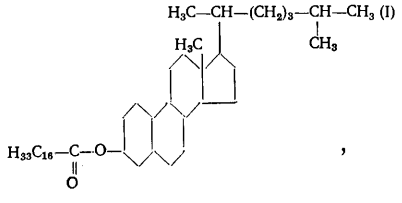
Liquid crystals have been used to separate the homologues of naphthalene[49], polynuclear aromatic hydrocarbons[50,51], steroids[52], polycyclic aromatic hydrocarbons up to C_{24}, [53] benzopyrene[54], herbicides[55], etc. A comparison has been made[56] of columns with bentonites and liquid crystals; it has been shown that the selectivity of liquid crystals with respect to *ortho*-, *meta*-, and *para*-isomers is in many instances greater. Theoretical problems concerning the selectivity of liquid crystals have been examined in a number of studies[36, 57-60].

One should note that accurate measurements, such as the determination of thermodynamic characteristics on liquid crystals[58,61-65], the determination of the orientational order in cholesteric[66] and nematic liquid crystals[67], the observation of a change in the selectivity and sorption capacity of the chromatographic column with liquid crystals following the application of an electric field[68-70], and the determination of the temperatures of transitions from one phase state of liquid crystals to another[58], can be carried out with the aid of chromatography.

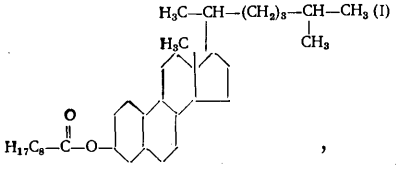
II. THE INFLUENCE OF VARIOUS FACTORS ON THE STRUCTURAL SELECTIVITY OF THERMOTROPIC LIQUID CRYSTALS

In all the studies quoted, except those of Zelenkova and coworkers[41,42], substances have been separated as a result of their dissolution in a film of liquid crystals deposited on an inert solid support, which hardly altered the properties of the liquid crystals and did not itself participate in the sorption of the components to be separated. We replaced the support with a low adsorption activity and a low specific surface ($s_{sp} \cong 1$ m^2 g^{-1}), usually employed, by a silica adsorbent support (silochrome) with $s_{sp} \cong 10$–150 m^2 g^{-1}.[71] It was assumed that, owing to the strong adsorption, there is a definite orientation of the polar molecules of the liquid crystal on the surface of the adsorbent support and that this rigidly fixed orientation persists over a wider temperature range due to the adsorption field of the adsorbent support. This made it possible, in its turn, to retain the selectivity of the liquid crystals with respect to isomers over a wide temperature range and for different amounts of liquid crystals.

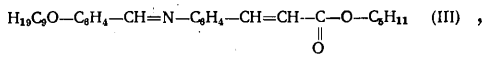
For this purpose, we used the adsorption–absorption variant of gas chromatography (GAAC),[72] which is intermediate between the gas-adsorption and gas-liquid variants and presupposes retention, as a result of both adsorption and dissolution (absorption), of the specimen in a film of liquid phase deposited on the adsorbent support. Nematic and smectic liquid crystals as well as cholesteric forms of nematic liquid crystals were investigated: cholesteryl oleate



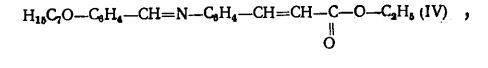
cholesteryl pelargonate



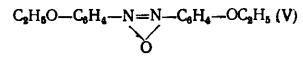
n-pentyl *p*-(n-nonyloxy)benzylidene-*p'*-aminocinnamate



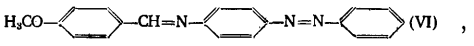
ethyl *p*-(n-heptyloxy)benzylidene-*p'*-aminocinnamate



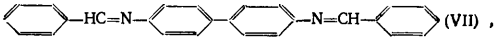
4,4'-diethoxyazoxybenzene



p-anisylideneaminoazobenzene



and *p,p'*-dibenzylidenebenzidine



The phase transition temperatures and the clarification temperatures t_{cl} of liquid crystals (I)–(VII) are listed below:

LC	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)
t, °C	19 (smc)	78 (smc)	80 (sosm)	120 (sosm)	135 (son)	147 (son)	234 (son)
t_{cl}, °C	33.5	91.5	135	156	165	183	260

(the following phase symbols are used for the specified phase transition temperatures: so = solid, sm = smectic, n = nematic, and c = cholesteric).

Specific macroporous adsorbent silochromes[73] with $s_{sp} = 120$, 150, 80, 50, 30, and 10 m^2 g^{-1}, a non-specific carbon adsorbent—PM-15 carbon black, and CaA molecular sieve ($s_{sp} \cong 800$ m^2 g^{-1}) were used as supports for the liquid crystals. The column size was 100×0.3 cm and the linear flow rate of nitrogen was 17 sm s^{-1}. For comparison, the liquid crystals were deposited also on the usual supports with a low activity: Chromaton ($s_{sp} = 1$ m^2 g^{-1}) and porous Teflon ($s_{sp} = 8$ m^2 g^{-1}).

Experimental measurements of the temperature variations to the retention volumes (V_g) on liquid crystals deposited on adsorbent supports confirmed the initial hypotheses. Fig. 1*a* presents the temperature variation of lg V_g of xylene isomers on cholesteryl pelargonate deposited on Chromaton ($s_{sp} \cong 1$ m^2 g^{-1}) in an amount of 6 wt.% (film thickness $\sigma \cong 60$ nm). Fig. 1*a* shows that the nature of these curves is consistent with the usual idea concerning the phase transition of liquid crystals when the temperature is varied, namely the plot shows clearly three regions of the phase states of cholesteryl pelargonate; solid, liquid crystal (mesophase), and liquid (isotropic region). The transition of cholesteryl pelargonate from the solid to the mesomorphic state is accompanied by a sharp increase of the V_g of the sorbates, i.e. at the melting point of 78 °C the retention times increase by a factor of ~5. In the region of the mesophase (78–91.5 °C) a further increase of temperature entails a decrease of V_g. In the transition of cholesteryl pelargonate to the isotropic liquid phase the retention parameters again increase but to a lesser extent. At the clarification point (91.5 °C) of the liquid crystal the selectivity of the separation (the factor α defined as the ratio of the corrected retention times of the *para*- and *meta*-isomers) diminishes. Whereas the values of V_g for the isomeric xylenes are similar in the region of the solid state of cholesteryl pelargonate and the isomers are not separated, in the region of the mesophase the V_g differ and the xylenes can be separated (Fig. 1*a*).

Thus the maximum selectivity of cholesteryl pelargonate with respect to the *meta*- and *para*-isomers is shown at the temperature where it undergoes a transition to the liquid crystal state and then decreases monotonically as the clarification point is approached. When the same amount of the liquid crystal (6 wt.%) is deposited on an active sorbent—Silochrome S-80 ($s_{sp} \cong 80$ m^2 g^{-1}) with a film thickness $\sigma \cong 0.7$, the nature of the phase transition curves changes markedly. Fig. 1*b* shows that in the region of temperatures corresponding to the transition of compound (II) to the mesophase no sharp and abrupt alteration of the retention parameters of the sorbates is observed. On the other hand, over the entire experimental range, an increase of temperature is seen to entail a decrease of the retention volumes. This

behaviour has also been observed[71] for monolayers of compounds (III) and (V) on Silochrome S-80.

The retention of a fairly high selectivity on such sorbents over the entire temperature range of the liquid crystal state of the given substance is of greatest interest. The initial adsorbent carrier does not separate xylene isomers and the selectivity in the separation is therefore due to the liquid crystal film. This unusual effect has been studied in detail in our investigations[71,74,75] for different ratios of the liquid crystal and the adsorbent carrier, i.e. a study was made of the influence of the thickness of the liquid crystal film on the effect of phase transitions; in addition the influence of the specific surface of the adsorbent carrier on this effect with retention of the chemical nature of the surface of the carrier was investigated in relation to both specific and non-specific adsorbents.

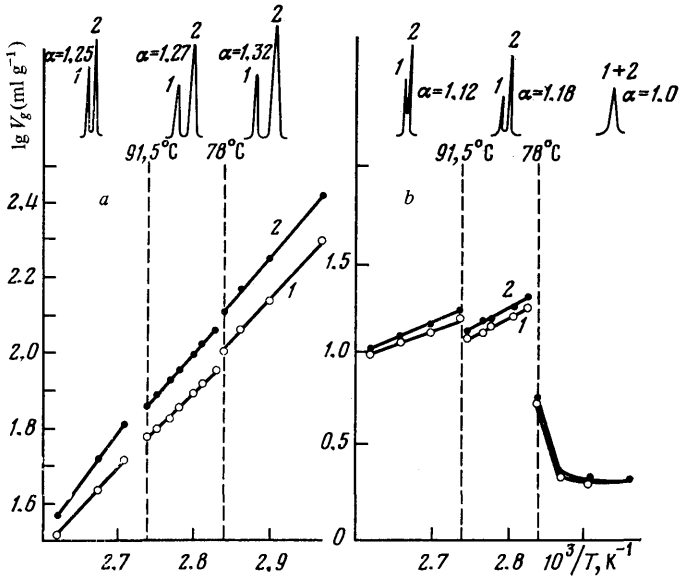


Figure 1. Temperature variation of the logarithms of the retention volumes (lg V_g) of xylene isomers on dehydroxylated Silochrome S-80 (*a*) and Chromaton (*b*) with 6 wt.% of cholesteryl pelargonate: 1) *m*-xylene; 2) *p*-xylene. The separation factors α for the pair of components at different temperatures are indicated[71].

It might have been supposed that the retention of a high selectivity obtains solely in the presence of small amounts of the liquid phase, i.e. for thin liquid crystal films, and that with increase of the film thickness on Silochrome S-80 a sharp increase of the retention parameters of the sorbates in the transition of compound (II) to the mesophase would be observed (as on a relatively inactive support—Chromaton). However, in the study of Silochrome S-80 specimens containing between 0.5 and 120 wt.% of compound (II) no breaks were observed in the relation between lg V_g and $1/T$. This can be explained by the fact that an increase of temperature does not lead to phase transitions, i.e. that the liquid crystal layers exist in the adsorbed state and that the adsorption energy exceeds the kinetic energy of the liquid crystal molecules corresponding to the given temperature.

At the liquid crystal clarification temperature there are also virtually no changes in the retention volumes.

Consequently the 6 wt.% of the liquid crystal on the surface of Silochrome S-80 has no phase transitions in the temperature range from 60° to 107 °C. The same behaviour of the liquid crystal has been observed also on Chromaton when a small amount of the liquid phase is deposited on its surface. For example, in the presence of 1 wt.% of the liquid crystal on Chromaton (Fig.2*a*) a virtually monotonic decrease of the retention characteristics with increasing column temperature is observed (by analogy with Silochrome). However, in this case the separation of xylene isomers is not observed even in the region of the mesophase.

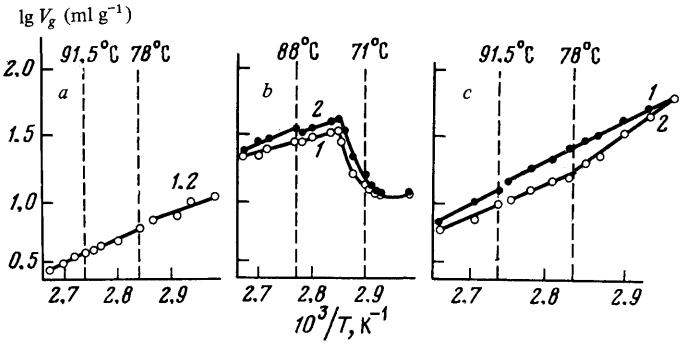


Figure 2. Temperature variation of lg V_g for xylene isomers on dehydroxylated Chromaton with 1 wt.% (*a*) and 12 wt.% (*b*) of cholesteryl pelargonate and on the same sorbent with 6 wt.% of aerosil dispersed in cholesteryl pelargonate (*c*):[74] 1) and 2) see Fig.1.

Similar relations have been observed by Gabitova and Vigdergauz[76] who noted a sharp decrease of the selectivity of the liquid crystal with respect to the *meta*- and *para*-isomers on reduction of the content of *p,p'*-ethoxymethoxyazoxybenzene on Chromosorb P to 1.2 wt.%. With increase of the content of compound (II) to 6 wt.% (Fig.1*a*) and to 12 wt.% (Fig.2*b*) on Chromaton, there is an abrupt increase of the retention characteristics on transition of the liquid crystal to the mesophase.

When the liquid crystal is deposited on Silochrome S-80 (an adsorbent with a high specific surface and a high adsorption potential), a definite orientation and ordering in the arrangement of the liquid crystal molecules on the surface of the adsorbent carrier apparently take place as a result of the adsorption field of the carrier. On further increase of the amount of liquid crystal on Silochrome, the molecules of the former are oriented relative to the liquid crystal molecules which have already been ordered. This orientation is probably close to the orientation of the molecules in the liquid crystal state and the selectivity of the separation is therefore high. As a result of the strong adsorption field of the surface of the adsorbent carrier, the ordered state persists over a wide temperature range (Fig.1*b*). Whereas the *meta*- and *para*-isomers of xylene are separated on Chromaton (Fig.1*a*) only at the melting point of compound (II), on Silochrome (Fig.1*b*) the xylenes are separated over the entire range of the specified temperatures.

Thus liquid crystals deposited in large amounts (in excess of 6 wt.%) on inert carriers with a low specific surface are selective only over a narrow temperature range, i.e. the temperature range of the anisotropic (mesomorphic) region is the only one where liquid crystals can be used. On the other hand, sorbents based on liquid crystals on an active adsorbent with a high specific surface are selective over a wide temperature range.

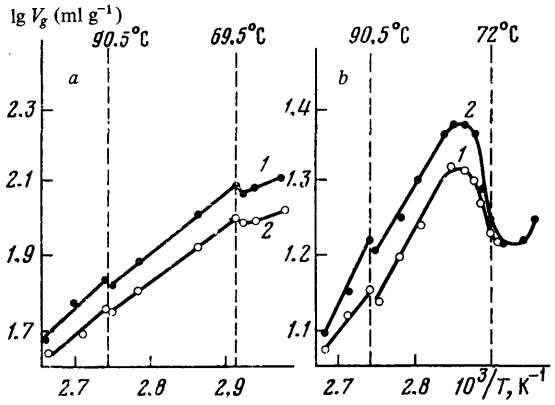


Figure 3. Temperature variation of lg V_g for xylene isomers on dehydroxylated Silochrome S-50 with 30 wt.% of cholesteryl pelargonate and on Silochrome S-10 with 6 wt.% of cholesteryl pelargonate[74]: 1) and 2) see Fig.1.

Apart from the high adsorption potential, the specific surface of the adsorbent support plays a major role in the attainment of a specific orientation and an ordered arrangement of the liquid crystal molecules. Fig.3 presents the temperature variation of lg V_g for xylene isomers on Silochrome with different values of s_{sp}. Thus, with decrease of s_{sp} of the Silochrome to 50 m^2 g^{-1} (Fig.3*a*) a large excess of the three-dimensional solid liquid crystal is already observed, which is indicated by the phase transition at 69.5 °C. There is also a phase transition at 90.5 °C, where the condensed film is transformed into a liquid. With decrease of s_{sp} of the Silochrome to 10 m^2 g^{-1} (Fig.3*b*), the nature of the curves representing the relation obeys the familiar hypothesis concerning the phase transitions of liquid crystals; however, the transition from the solid state to the mesophase is not so sharp as in the case of Chromaton (Fig.1*a*).

The temperature variation of the structural selectivity has been obtained[74] for liquid crystal (II) deposited on carriers with different values of s_{sp}; the maximum separation factor α is observed for compound (II) deposited on Silochrome S-150 ($s_{sp} = 153$ m^2 g^{-1}).

The influence of the chemical nature and geometrical structure of the adsorbent carrier surface on the mesomorphic state of a thermotropic liquid crystal has been investigated[74]. The temperature variation of the retention characteristics of xylene isomers was investigated on Silochromes—adsorbents of the same type but with different chemical surfaces (hydroxylated, dehydroxylated, and silanised Silochromes)—modified with cholesteryl pelargonate. On the silanised Silochrome S-180 with a liquid crystal monolayer (6 wt.%), it was observed that the xylene isomers are not separated over the entire specified temperature range (Fig.4*a*). This can be explained by the fact that the silanised (i.e. treated with hexamethyldisilazane) Silochrome is non-polar and that the adsorption of liquid crystal molecules on it is greatly reduced in contrast to the hydroxylated Silochrome; therefore, for a liquid crystal content of 6 wt.%, an ordered orientation of the liquid crystal molecules on the adsorbent surface does not take place and the xylene isomers are not separated. On the Silochrome hydroxylated to the maximum extent (continuous coverage by OH groups) with a monolayer of compound (II) (Fig.4*b*), the xylene isomers are separated just as completely as on the dehydroxylated Silochrome (OH groups removed from the surface by heat treatment at

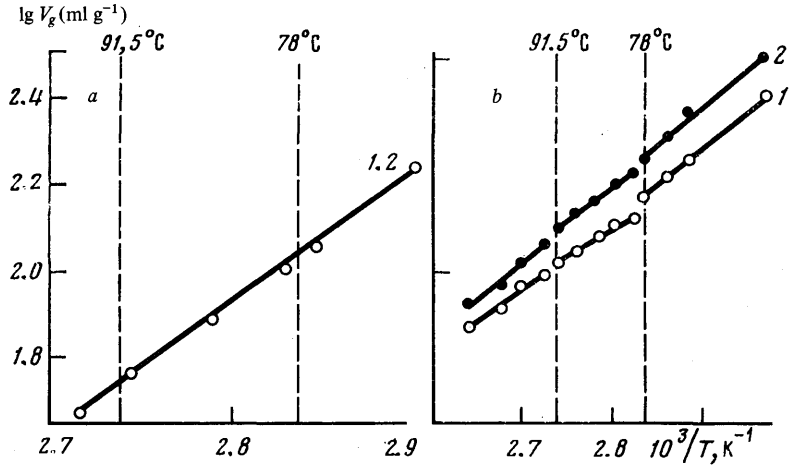


Figure 4. Temperature variation of lg V_g for xylene isomers on silanised (*a*) and hydroxylated (*b*) Silochrome S-80 with 6 wt.% (*a*) and 15 wt.% (*b*) of cholesteryl pelargonate[74]: 1) and 2) see Fig.1.

1000 °C) (Fig.1*b*). This finding confirms the hypothesis that, for the ordered parallel arrangement of the liquid crystal molecules, the nature of the surface, i.e. the nature of the adsorption forces of the adsorbent support, plays a major role.

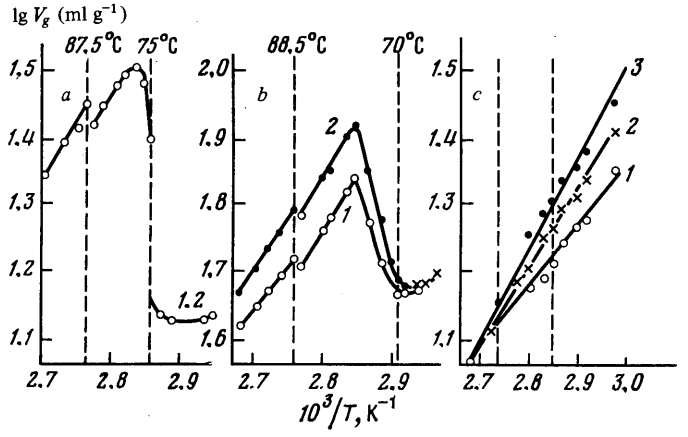


Figure 5. Temperature variation of lg V_g for xylene isomers on porous Teflon with 6 wt.% of cholesteryl pelargonate (*a*), PM-15 carbon black with 25 wt.% of cholesteryl pelargonate *b*), and CaA molecular sieve with 6 wt.% of cholesteryl pelargonate (*c*):[74] 1)–3) *m*-, *p*-, and *o*-xylenes respectively.

Fig.5 presents the temperature variation of lg V_g on carriers exhibiting marked chemical differences. Thus, on porous Teflon (a non-polar adsorbent with a weakly adsorbing surface) there is a distinct transition of the liquid crystal from the solid to the mesomorphic state, but the xylene isomers are not separated even in the region of the mesophase (Fig.5*a*). When the support is replaced by a non-specific carbon adsorbent—the PM-15 carbon black ($s_{sp} = 15$ m^2 g^{-1}), there is no sharp and abrupt change in the retention parameters (Fig.5*b*). In this case the fusion of the liquid crystal takes place gradually and not abruptly, the melting point of the liquid crystal being displaced towards lower temperatures. This can be explained by the fact that the liquid crystal film on the surface of the carbon adsorbent is acted upon by its adsorption field and the physical properties of the film therefore differ from those of the bulk-phase liquid[77]. When the CaA molecular sieve ($s_{sp} \approx 800$ m^2 g^{-1}) is used as the support for a thin film of compound (II), phase transitions at 78° and 91.5 °C are not observed and the liquid crystal exists in the form of a "condensed" film (Fig.5*c*). At 95 °C and above the liquid crystal does not exhibit selectivity with respect to the *meta*- and *para*-isomers, which apparently indicates the absence of an oriented arrangement of the liquid crystal molecules on the surface of the CaA molecular sieve. In the range 60–95 °C the selectivity of the liquid crystal decreases monotonically.

When silica (aerosil) was introduced into the liquid crystal in proportions of 1:1, i.e. on deposition of 6 wt.% of the liquid crystal and 6 wt.% of aerosil on Chromaton, appreciable phase transitions at 78° and 91.5 °C were not observed either (Fig.2*c*), and the behaviour was analogous to that observed on deposition of 30 wt.% on Silochrome S-80. However, the maximum selectivity occurs only at 78 °C (Fig.2*c*).

Thus the high structural selectivity with respect to positional isomers, the low viscosity in the region of the nematic and smectic mesomorphic states, and the high thermal stability of certain liquid crystals make it possible to recommend them for the separation of complex chemical compounds.

III. THE PHASE TRANSITIONS IN THE MESOMORPHIC STATE OF A SMECTIC LIQUID CRYSTAL

Several modifications of thermotropic smectic (soap-like) liquid crystals (SLC) can be distinguished[78]. The smectic mesophase A (S_A) consists of layers freely mobile relative to one another. The mesophase S_A is the highest-temperature phase and is least "organised" among the SLC. The smectic mesophase B (S_B) is more ordered than S_A. The smectic mesophase C (S_C) is analogous to the mesophase S_A but differs from it by the inclination of the molecular axes.

In addition to the physical methods for the investigation of liquid crystals, it is possible to employ the GAAC variant to study the phase transitions in SLC in the mesomorphic state. A study of the retention characteristics of xylene isomers on liquid crystal (III) deposited on Chromaton in an amount of 10 wt.% showed[79] that this SLC exhibits polymorphism (Fig.6*a*), namely in the region of the mesomorphic state (80–134 °C) the plot shows three breaks corresponding to the smectic states A, C, and S. As stated above, the phase states A, C, and S differ from one another by the different arrangements of the molecules in the smectic layers[78] and in this connection a triple increase of the retention parameters of the sorbate is observed.

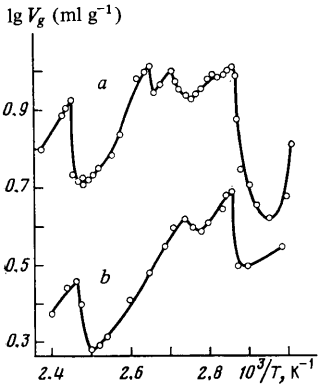


Figure 6. Temperature variation of lg V_g for *p*-xylene on dehydroxylated Chromaton with 10 wt.% (*a*) and 3 wt.% of n-pentyl *p*-(n-nonyloxy)benzylidene-*p*-aminocinnamate[79].

The polymorphism of the liquid crystal state of the test substance has been confirmed by microscopic and differential thermal (DTA) analyses. Fig.7 presents the heating and cooling thermograms for liquid crystal (III); the peak at 93 °C, corresponding to the transition from one liquid crystal modification to another, is clearly visible[79]. The peaks on the thermogram at 74° and 135 °C correspond to fusion and the transition to the isotropic liquid. It follows from the DTA that the substance has two modifications. However, microscopic analysis (Fig.8) demonstrated the presence of

three modifications. Yet another polymorphic transition occurs at 101 °C. According to Sackmann's classification[80], the test substance has smectic A, C, and S modifications which exist in the temperature ranges 135–101 °C, 101–93 °C, and 93–74 °C respectively (Fig.8). It may be that the S_A–S_C transition, which is not shown by the DTA curve of the second kind, or at any rate the thermal effect corresponding to this transition, is small.

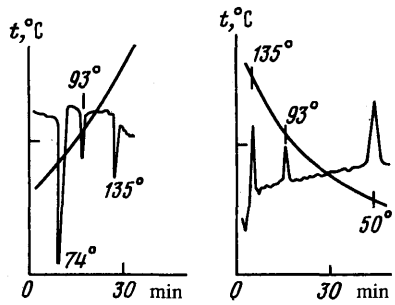


Figure 7. Heating and cooling thermograms for n-pentyl *p*-(n-nonyloxy)benzylidene-*p'*-aminocinnamate[79].

With decrease of the content of liquid crystal on Chromaton, i.e. in the case of a thin film (Fig.6*b*), the plot shows only two breaks. Fig.6*b* also shows that, with decrease of the amount of liquid crystal on the solid carrier, the phase transition temperature shifts towards lower values and the selectivity with respect to positional isomers falls. Similar features have been observed[76] in a study of the thermotropic liquid crystal *p*-methoxyethoxyazoxybenzene.

IV. ASSESSMENT OF LIQUID CRYSTAL STATIONARY PHASES ON THE BASIS OF POLARITY FACTORS

The existing methods for the estimation of the polarities of stationary phases have been examined in fair detail in a number of reviews[81–83]. Among all the known methods, the procedure proposed by Rohrschneider[84] and improved by McReynolds[85] has received the greatest recognition. It was of interest to assess the liquid crystals investigated in terms of selective properties as stationary phases (SP) with unique chromatographic properties.

We attempted[86] to classify such variable-selectivity sorbents by analogy with the methods used in gas–liquid chromatography. The possibility of using Brown's method[87] and the system of Rohrschneider's polarity factors[88] was tested on the basis of experimental results. According to Rohrschneider[88], the difference between the Kovats indices[89] on the test and standard stationary phase is a measure of the polarity of the stationary phase.

We determined the polarities of sorbents based on Silochromes and liquid crystals as the differences between the Kovats indices on squalane and the test sorbent:

$$\Delta I = I_{test} - I_{sq} \quad .$$

The overall quantity

$$\sum \Delta I = ax + by + cz + du + es \qquad (1)$$

characterises the polarity of the stationary phase and the components of the sum represent the degree of interaction of each reference substance (benzene, ethanol, ethyl methyl ketone, nitromethane, and pyridine) with the stationary phase. The polarity coefficients of the substances analysed (*a*, *b*, *c*, *d*, and *e*) must remain constant on different stationary phases[90]. In estimating the selectivity of stationary phases for the separation of positional isomers, Vigdergauz et al.[91] introduced and additional term into Eqn.(1), characterising the selectivity of the mesophase with respect to the *meta*- and *para*-isomers.

The polarity factors for different phase states of the following liquid crystals have been determined[86] by Eqn.(1): (II), (V), and (III). The results are in Table 1. For comparison, the table also includes the polarity factors for the adsorbent supports.



Figure 8. Textures of the liquid crystal state of n-pentyl *p*-(n-nonyloxy)benzylidene-*p'*-aminocinnamate[79].

As already mentioned, the nature of the curves for the temperature variation of V_g of several isomers of organic compounds is inconsistent with the classical concept of the phase transitions in liquid crystals as a function of temperature, namely that the retention characteristics diminish with increasing column temperature. Indeed, Table 1 shows that the polarity factors of Silochrome S-80 containing a monomolecular layer of cholesteryl pelargonate (0.754 mg m^{-2}) diminish with increasing column temperature.

Table 1. The polarity factors (x, y, z, u, and s) and the conventional chromatographic polarities (P) of sorbents based on silicas and liquid crystals (standard—squalane, t—column temperature).

LC	t, °C	x	y	z	u	s	P
			Silochrome S-80				
—	200*	1.30	7.36	8.05	5.04	9.20	31
—	200	0.40	4.05	5.80	3.15	6.90	8
(III)	100	0.21	5.06	3.43	2.31	2.92	12
(III)	135	0.26	5.16	2.88	2.43	3.80	10
(III)	165	0.30	6.16	2.86	2.23	5.21	6
(II)	63	0.26	4.14	2.93	2.89	—	28
(II)	78	0.17	2.36	2.86	0.84	—	14
(II)	91.5	0.01	1.81	2.10	0.73	—	11
			Chromaton				
(V) **	63	1.55	3.35	2.19	3.78	3.40	28
(V) **	120	1.51	2.96	2.13	3.53	2.67	20
(V) **	150	1.75	2.16	2.21	3.55	2.87	18
(II) ***	63	0.26	4.14	3.03	2.79	—	27
(II) ***	78	0.34	4.70	3.83	3.86	—	29
(II) ***	91.5	0.31	3.40	4.07	3.32	—	15

*A hydroxylated adsorbent carrier was used, while in the remaining cases the carrier was dehydroxylated.

**$a_{LC} = 0.052$ mg m^{-2}.

***$a_{LC} = 0.009$ mg m^{-2}; in the remaining cases $a_{LC} = 0.754$ mg m^{-2}.

The system of Rohrschneider's coefficients constitutes a classification where, apart from the electron donor–electron acceptor activity, account is taken of the proton donor–proton acceptor activity of the phases in relation to the sorbates as well as the orientation interaction between them. Thus the polarity factors of the electron donor and acceptor characterising the retention of benzene (x) and nitromethane (u) diminish sharply on transition of compound (II) from the solid to the liquid crystal state and further to the isotropic liquid. The polarity factors of the proton donor characterising the retention of ethanol (y) change sharply on transition of this liquid crystal from the solid to the mesomorphic state.

The conventional chromatographic polarity of this sorbent (Table 1), which we estimated in relation to a specific pair of compounds (benzene–cyclohexane), also decreases with increase of column temperature. On the same liquid crystal deposited on the inert carrier Chromaton, higher polarity factors are observed at the point corresponding to the transition of the liquid crystal from the solid to the mesomorphic state (78 °C); the retention characteristics, particularly the retention times, then increase by a factor of ~5. At 78 °C the conventional chromatographic polarity is also a maximum.

Comparison of the polarity factors on hydroxylated and particularly on dehydroxylated Silochromes with those for the same Silochromes modified by liquid crystals shows that on the latter the polarity factors decrease markedly, especially the polarity factor z (for ethyl methyl ketone) characterising the orientational interaction. Among the initial Silochromes, a high capacity for orientational interaction has been observed for the hydroxylated Silochrome with an intact coating of hydroxy-groups on its surface, which is classified as a type II adsorbent in Kiselev's classification[92]. While the polarity factors s are exceptionally high, the constant a, characterising the dispersion interaction on the hydroxylated Silochrome, is low. A change in the chemical properties of the surface of hydroxylated Silochrome, namely its dehydroxylation (by heat treatment at 1000 °C) and modification with liquid crystals, leads to a sharp decrease of all the polarity constants.

Together with the Rohrschneider method, whereby one can take into account different intermolecular interactions, Brown's method[87] has been applied. Brown was the first to apply the triangular Gibbs–Roozeboom diagram to gas chromatography for a clear estimate of the properties of the stationary phases. This method provides for the use of a triangular graph along the axis of which one plots the retention fractions representing the ratios of the specific retention volume of one of the reference sorbates to the sum of the volumes of three reference sorbates. The following systems have been used for the latter: n-hexane–ethanol–ethyl methyl ketone or n-hexane–nitromethane–pyridine, i.e. nonpolar compound—electron donor–electron acceptor systems.

When the retention of all the elements is determined from a single chromatogram, the retention fraction can be calculated directly from the corrected retention times (t_r):[93]

$$F = t_r/(t_r' + t_r'' + t_r'''). \qquad (2)$$

For the initial and liquid crystal-modified silicas, the retention fraction of ethyl methyl ketone is greatest; consequently, the donor–acceptor interaction makes the main contribution to the retention. In addition, we demonstrated the possibility of using pyridine, a stronger electron donor, and nitromethane, a stronger electron acceptor, as reference sorbates together with n-hexane. For all the sorbent specimens, the retention fractions of pyridine are highest, which again demonstrates the dominant contribution of sorbate–sorbent donor–acceptor interactions to the retention.

Table 2. The polarity factors of certain stationary phases and sorbents based on Chromaton and SLC (V).

SP, sorbent	t, °C	x	y	z	u	s
OV-17	100	2.08	3.85	2.62	5.33	3.45
Sorbent	63	1.55	3.35	2.19	3.78	3.40
SKTF-100	100	1.57	4.96	2.05	3.13	2.17
Sorbent	120	1.51	2.96	2.13	3.53	2.67
OS-124	100	1.75	2.27	2.34	3.26	2.84
Sorbent	150	1.75	2.16	2.12	3.55	2.87

In order to estimate the possibility of the practical application of the polarity constants found for sorbents based on silicas and liquid crystals, it is necessary to compare the results with the literature data for known stationary phases. Such a comparison makes it possible to discover analogues of stationary phases and to illustrate the possibility of replacing the latter by sorbents based on silicas and liquid crystal systems. For comparision, use was made of data of

Subina[94], who characterises in terms of polarity the stationary phases most frequently used in gas chromatographic practice. As an illustration, Table 2 presents some of these data. It shows that the sorbent based on Chromaton and liquid crystal (IV) in a single chromatographic column at different temperatures and hence in different phase states can replace three sorbents: polyphenyl ester OS-124, SKFT-100, and OV-17.

Thus the use of liquid crystals as stationary phases makes it possible to reduce the number of stationary phases used in gas chromatography without diminishing the range in which selectivity can be regulated. Furthermore, the assessment of silica adsorbents and modified sorbents based on them, carried out on the basis of the retention characteristics of reference compounds, permits a well founded approach to the selection of a modified sorbent for the solution of a specific analytical problem.

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Oxidation of Ketones by Molecular Oxygen

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The results of fundamental studies on different methods of oxidising aldehydes and ketones by oxygen are presented; the purely thermal oxidation, the photochemical oxidation, as well as the low-temperature oxidation in alkaline media are considered. The general postulates of the reaction mechanisms are described and specific instances involving aliphatic, alicyclic, saturated, and aromatic ketones as well as the mechanisms of the decomposition of the hydroperoxides of α-ketones are surveyed.
The bibliography includes 101 references.

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I. INTRODUCTION

The present author's two previous papers were devoted to various methods of oxidising alcohols[1] and phenols[2]; it is logical to examine also carbonyl compounds from this point of view. Indeed they are intermediates in the oxidation of hydrocarbons and are formed when animal or plant lipids are subjected to aerobic heat treatment. It is known that alcohols and carbonyl compounds (aldehydes or ketones depending on the structure of the hydrocarbons) are formed simultaneously in the oxidation of hydrocarbons via intermediate hydroperoxides; more carbonyl compounds are formed in the subsequent oxidation of the alcohols.

The mechanism of the formation of carbonyl compounds in the oxidation of hydrocarbons has been described in detail in reviews[1-3].

The main products of the oxidation of carbonyl compounds are carboxylic acids formed via chain dissociation or without such dissociation, depending on the initial compound—ketone or aldehyde. Different methods for the oxidation of carbonyl compounds are not only of theoretical but also of considerable practical interest for the synthesis of carboxylic acids and their derivatives by the oxidation of hydrocarbons, particularly for the synthesis of dibasic acids from alicyclic hydrocarbons.

The formation of mono- and poly-functional saturated and unsaturated carbonyl compounds from derivatives of oleic, linolenic, and linoleic acids has been described in detail in review articles[4-6]. Furthermore, numerous carbonyl compounds form part of the composition of natural products and are an important raw material for various branches of the manufacture of chemical products—solvents, pharmaceuticals, perfumes, dyes, and plastics.

It is noteworthy that methods for the oxidation of aldehydes in the liquid or vapour phase have now been described in fair detail (the latest review was published in 1976). Thus the liquid-phase oxidation of aldehydes has been described[7]; a review devoted to the mechanism and kinetics of the oxidation of aldehydes in the liquid and vapour phases has been published[8]. The photochemical oxidation of aldehydes in the liquid or vapour phase has been considered by Niclause and Lemaire[9], Maslov and Blyumberg[10] discussed in detail the liquid-phase oxidation of aldehydes and their joint oxidation with olefins. Elkik[11] described the mechanism of the oxidation of aldehydes in alkaline media.

Apart from the reviews listed above, the results of individual investigations during the last 26 years have been the subject of very detailed publications and in many instances noteworthy conclusions concerning the kinetics of the processes are presented.

Thus Combe et al.[12] published two papers on the oxidation of acetaldehyde and propionaldehyde in the vapour phase (certain considerations concerning the kinetics are presented and the experimental methods are described in detail). Lemaire[13] investigated the photochemical oxidation of C_7 aldehydes by infrared spectroscopy and Deglise[14] studied the photochemical oxidation of crotonaldehyde. The paper of Franck et al.[15], devoted to the liquid-phase oxidation of benzaldehyde, presents conclusions concerning the process kinetics and critical comments on previous studies. The autoxidation of furfural has been examined by Isacescu et al.[16], whose paper also contains an extensive historical review and a critical examination of early investigations.

Extensive review articles devoted to the oxidation of aldehydes of different types in volume VII of Grignard's collection[17-20] are noteworthy; they also deal with the oxidation reactions of aliphatic[17], alicyclic[18], aromatic[19], and unsaturated (mono- and poly-olefinic and acetylenic)[20] aldehydes.

Thus, since the methods for the oxidation of aldehydes have been described and discussed in a whole series of reviews (most of which were published in 1976) and original publications, the author believes that there is no need to consider them within the framework of the present survey.

The literature on the oxidation of ketones differs appreciably from that on aldehydes. As far as the present author is aware, there are only two reviews on the purely thermal[21] and vapour-phase[22] oxidations; the latter paper deals with various photochemical reactions in the vapour phase and with general postulates concerning the photochemical oxidation mechanism. However, the above reviews[21,22] do not deal either with the purely thermal liquid-phase oxidation of ketones in the presence of various catalysts or in their absence (there are only short sections in the general reviews on organic peroxides[23-25] with references up to 1960) or with their oxidation in an alkaline medium at a low temperature, which has been the subject of numerous detailed investigations in the last decade. The low-temperature oxidation in an alkaline medium proved to be highly effective, since it makes it possible not only to synthesise and isolate various

α-keto-t-hydroperoxides but also to investigate their properties, in particular their radical (in the liquid and vapour phases) and ionic decompositions catalysed by alkali.

It is noteworthy that individual ketones form part of the composition of many natural essential oils, sex hormones, and wood tar. It is known that methyl ketones CH_3COR (R represents an odd number of carbon atoms ranging from C_3 to C_{11}) are formed when saturated lipids become rancid and by the action of certain moulds on saturated aliphatic acids, their ammonium salts, and triglycerides, and also that ketones and aldehydes of various types are produced in the course of the thermal oxidation of lipids[4-6].

Data on the industrial applications of methyl ketones have been described by Miller[26].

A review article[27] on ketones and an article in volume VII of Grignard's collection[28-31], which deals with the synthesis and reactions of saturated aliphatic[29], ethylenic[30], and acetylenic[31] ketones are noteworthy. Turro's paper[32] is devoted solely to cyclopropanone and its derivatives and that of Srinivasan[33] deals with the photochemistry of cyclic ketones.

Various chemical and physical aspects of the ketone oxidation reactions are fairly interesting, particularly the studies of the last decade; therefore, from our point of view, it is appropriate to survey the literature data on the methods of oxidising ketones in addition to the information about the reactions of these compounds already available.

II. GENERAL POSTULATES

1. Thermal Oxidation under the Influence of O_2 in a Neutral Medium

Jenkins[34] claims that many ketones having the general formula $XC_6H_4-CH_2-COR$ acquire the smell of an aldehyde on simple storage at room temperature in the presence of atmospheric oxygen or in sunlight. He was unable to obtain *o*-chlorobenzoic acid and benzaldehyde from benzyl *o*-chlorophenyl ketone.

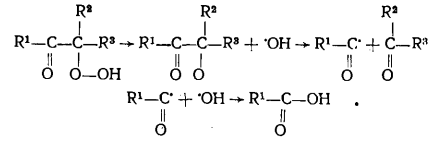
Scharp et al.[35] isolated butyric acid and propionaldehyde in the thermal autoxidation of dipropyl ketone at 110–120 °C. Furthermore, the authors noted the formation of a peroxide, whose content increases (primarily as a function of reaction time), passes through a maximum, and then falls (as in the oxidation of hydrocarbons of various types and other organic compounds); this is not observed for the extent of conversion to aldehyde and acid, which increases continuously. The same workers[36] isolated acetone and isobutyric acid after the thermal autoxidation of di-isopropyl ketone at 100° and 110 °C. It is of interest to note that in the first instance (in the presence of a secondary carbon atom conjugated with C=O) a small amount of water is formed and part of the aldehyde is converted into the corresponding acid.

It has been shown[37] that in the thermal autoxidation of certain alicyclic ketones (cyclohexanone and α- and β-tetralinones) at temperatures from 75° to 100 °C peroxide is formed initially and then, as a consequence of ring rupture, the corresponding aldehydoacids.

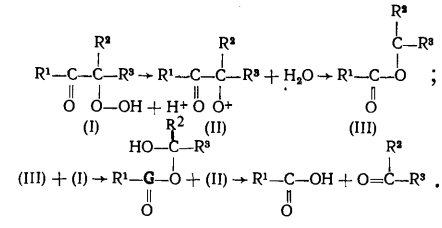
The experimental results obtained for several aliphatic, benzyl, and alicyclic ketones have shown that molecular oxygen initially acts (at least to a large extent) on the carbon atom in the α-position relative to the C=O group, which leads to the formation of the ketohydroperoxide $R^1C(=O)C.[(OOH)(R^2)(R^3)]$, which then decomposes into an aldehyde and carboxylic acid with dissociation of the O–O and C–C bonds in the C–C=O group.

As in the general case of hydrocarbons of various types, the rate of oxidation and stability of the hydroperoxides increase on passing from a secondary to a tertiary carbon atom.

The decomposition of the hydroperoxide proceeds mainly via a radical mechanism:



and then via an ionic mechanism, the process being catalysed by the acid formed:



Indeed it has been shown[38] that in the case of cyclohexanone the rate of decomposition of the hydroperoxide formed greatly increases after the introduction of acetic acid. The formation of acid is then clearly autocatalytic, as for dipropyl ketone at 120 °C; the acid content is low during the first 5 h after the start of reaction and then it reaches 0.022 and 0.080 mole per mole of the ketone after 8 and 12 h respectively[39].

Table 1. The autoxidation of ketones.

Ketone	*t*, °C	Time, h	Content of oxidation products, moles per mole of initial ketone		τ*, h	Refs.
			peroxide	acid		
Di-isopropyl ketone	85	8	0.022	0.0148	—	[40]
Di-isopropyl ketone	100	36	0.05	0.05	6	[36]
Di-isopropyl ketone	110	16	0.040	0.040	0	[36]
Dipropyl ketone	110	24	0.005	0.05	8	[35]
Dipropyl ketone	120	6	0.01	0.02	—	[35]
Ethyl methyl ketone	120	10	0 003	0.003	—	[39]

*τ is the induction period in the formation of the acid.

Table 1 presents quantitative data for the formation of hydroperoxides and acids from three ketones at different temperatures.

The method of acid-catalysed ionic decomposition of hydroperoxides was first developed[40] in relation to the decomposition of decalinyl hydroperoxide in the presence of H_2SO_4; the decomposition of cumenyl-hydroperoxide to phenol and acetone proceeds via the same mechanism[41], which has been discussed in detail by Tobolsky and Mesrobian[42].

We may note that, apart from the main pathway involving the rupture of the bond in the α-position relative to the C=O group, there is also a possibility (to a much lesser extent) of the dissociation of the bond in the β-position, particularly if the group in the β-position relative to C=O is an H atom (the formation of H_2O) or $H_2CC_6H_4X$. Thus

although the action of O_2 on the carbon atom in the α-position relative to the C=O group constitutes the main pathway, it is not the only one: carbon atoms in other positions can also be acted upon by oxygen, as has been demonstrated for long-chain ketones.

Indeed Rif and coworkers showed in relation to the oxidation of 2-octanone[43] and 6-undecanone[44,45] that, apart from the compounds formed as a result of the dissociation of the chain in the α-position, several other substances are formed as a consequence of the dissociation of the chain in other positions.

2. The Effect of O_2 in the Presence of Ionising Radiation in a Neutral Medium

The photochemical oxidation of acetone and diethyl ketone under the influence of light at wavelengths in the range $267 < \lambda < 313$ nm at different temperatures has been the subject of numerous investigations which have been analysed by Bernard[21]. It has been shown that the primary reaction step consists in the formation of the radicals $R^2-\dot{C}=O$ (or $R^1-\dot{C}=O$ and $\dot{R}^2$), which are oxidised to the corresponding peroxy-radicals.

The final products are formed from the radicals $R^1O-\dot{O}$, $R^1-\dot{O}$, $R^2-C(=O)O\dot{O}$, and $R^2-(C=O)-O^{\cdot}$ and constitute a mixture of CO, CO_2, the acids R^1-COOH and R^2-COOH, as well as alcohols and aldehydes formed as a consequence of the disproportionation of the radicals $R^1O^{\cdot}$ and $R^2O^{\cdot}$.

3. The Effect of O_2 in an Alkaline Medium

Ketones can react with molecular oxygen also at a very low temperature in a highly alkaline medium in aprotic solvents with formation (as in a neutral medium) of an α-ketohydroperoxide as the primary product. The rate of reaction depends very markedly on the configuration of the carbon atom in the α-position relative to the C=O group. Thus it is very low for the primary carbon atom and very high for secondary and tertiary carbon atoms. However, in the former case the yield of hydroperoxides is low, since they rapidly decompose in an alkaline medium; in the case of a tertiary carbon atom it is possible to isolate hydroperoxides with a higher degree of purity and in a high yield.

The selection of temperature and reaction time is very important for the attainment of the maximum yield. (t-Hydroperoxides also decompose under the influence of alkali via the general mechanism $2ROOH \rightarrow 2ROH + O_2$ but at a much lower rate than secondary hydroperoxides[23].) It is noteworthy that in asymmetric ketones of the type $H_3C-(C=O).CH(CH_3)_2$ only the tertiary group is involved. We may note that the oxidation in a highly alkaline medium is possible not only for ketones but also for many other organic compounds with a tertiary α-carbon atom, for example, ethers, esters, nitriles, hydroxylamines, hydrazines, mercaptans, and phenols.

The influence of the solvent on the yield of hydroperoxide has been studied[46] in relation to isopropyl methyl ketone in the presence of the $(CH_3)_3COK/(CH_3)_3COH$ system at −8° for a reaction time between 4 and 10 min. It was shown that the yield of hydroperoxide decreases in the sequence dimethylformamide > dimethoxyethane > hexamethylphosphoramide > tetrahydrofuran > acetonitrile > toluene > acetic acid, the yields being in proportions of 87, 80, 72, 66, 56, 48, and 38% respectively.

Evidently in the first two solvents the reaction proceeds even in the presence of aqueous solutions of alkalies, while in others it is necessary to use stronger bases (such as alkoxides) and in aprotic solvents such as diglyme and hexamethylformamide the rate of reaction is much higher than in $(CH_3)_3COH$.

The first reaction stage is the ionisation of the initial compound (designated by RH) by the base $\ddot{B}$ with formation of the anion R^-, which then reacts with molecular oxygen:

$$RH + \ddot{B} \rightarrow R^- + BH \ ;$$

$$R^- + O_2 \rightarrow R^{\cdot} + {}^{-}O_2^{\cdot} \ ;$$

$$R^{\cdot} + O_2 \rightarrow RO-O^{\cdot} \xrightarrow{HR} RO-OH + R^{\cdot} \ .$$

Consequently this reaction involves the formation of the O_2^- radical-ion the properties and formation of which in the course of various chemical reactions have been described in a recent review[47].

The kinetic data and the mechanism of the oxidation in an alkaline medium, which is applicable to substances other than ketones, particularly to esters[48] and alkyl halides[49], have been discussed in detail in the literature.

III. OXIDATION OF SATURATED ALIPHATIC AND AROMATIC KETONES

The thermal oxidation of acetone has been the subject of numerous studies. Acetone contains only primary carbon atoms in the α-position relative to the C=O group; it is fairly resistant to the action of atmospheric oxygen and reacts with the latter (in the absence of any oxidation initiators) only above 250 °C, so that its thermal oxidation can be studied only in the vapour phase. Such oxidation has been the subject of two serious investigations[50,51] carried out using specially purified acetone in the temperature range 250–500 °C at acetone and oxygen pressures of 60 and 30 mmHg respectively. The reaction products were determined quantitatively and qualitatively at 284° and 498 °C. It was shown that at these temperatures considerable amounts of H_2O and CO are formed. On the other hand, the contents of CO_2 and HCHO are considerable at 284 °C and very low at 498 °C; furthermore, methane (in fairly large amounts) and ethyl methyl ketone (in much smaller amounts) are formed only at the latter temperature. At 284 °C there is an appreciable amount of methyl hydroperoxide (which was not detected at 498 °C) and also a very small amount of H_2O_2, H_2, CH_3OH, and OCH–CHO. These compounds are formed in accordance with the equations presented below, the first of which describes the reaction at 284 °C and the second at 498 °C:[50,51]

$$(CH_3)_2C=O+2.5O_2 \rightarrow 1.75H_2O+1.25CO+0.65CO_2+0.6CH_3\dot{O}OH + \\ + 0.5HCHO+0.1H_2 \ ;$$

$$(CH_3)_2C=O+O_2 \rightarrow 0.9H_2O+1.6CO+0.7CH_4 \\ + 0.3HCHO+0.07(C_2H_4+CO_2+H_2) \ .$$

The ratio of the contents of the same compounds (r) formed at 284° and 498 °C is 2 for H_2O, 0.8 for CO, and 9.3 for CO_2.

The results suggest the following reaction mechanism; in the first step, as in the liquid-phase autoxidation of ketones, at 498 °C hydrogen is abstracted from acetone with formation of a radical:

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + O_2 \rightarrow CH_3-\underset{\underset{O}{\|}}{C}-\dot{C}H_2 + {}^{\cdot}O-OH \ .$$

Its life is very short; it decomposes to keten and the radical $H_3C^{\cdot}$ before reacting with O_2:

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2^{\cdot} \rightarrow H_3C^{\cdot} + C\overset{\overset{O}{\|}}{=}CH_2 \ .$$

In the presence of O_2, keten decomposes almost exclusively to H_2O and CO with traces of CO_2 + C_2H_4, while $H_3CO-O^{\cdot}$ is formed from the radical $H_3C^{\cdot}$. The behaviour of this radical also depends on temperature: at an elevated temperature (498 °C) it decomposes mainly to H_2O and the $\dot{C}HO$ radical:

$$CH_3O-O^{\cdot} \rightarrow H_2O + H-\overset{\overset{O}{\|}}{C}^{\cdot} \ .$$

The latter can in its turn either recombine with formation of glyoxal or can react with O_2; in the latter case the products are CO and the radical $HOO^{\cdot}$:

$$H-\overset{\overset{O}{\|}}{C}^{\cdot} + O_2 \rightarrow CO + HO-O^{\cdot} \ .$$

The radical $HOO^{\cdot}$ can abstract hydrogen from acetone to form the radical $CH_3COCH_2^{\cdot}$ and H_2O_2.

At 284 °C the radical $H_3CCO^{\cdot}$ mainly abstracts hydrogen from acetone or HCHO to form CH_3CHO, partial decomposition of which yields HCHO and H_2O; the radical $CH_3COCH_2^{\cdot}$, whose lifetime at 284 °C is longer than at 498 °C, mainly reacts with CO_2 to form a radical which subsequently decomposes by the mechanism

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2O-O^{\cdot} \rightarrow CH_3^{\cdot} + CO_2 + HCHO \ .$$

The photochemical oxidation of acetone (particularly at λ = 313 nm) in the vapour phase in the range from room temperature to 250 °C and at different oxygen and acetone pressures has been described in extensive reviews[52-65] and the conclusions reached in them have been analysed in detail in Hoare's review[22]. The liquid-phase photochemical oxidation of acetone at 30 °C has also been studied[64].

In these investigations it has been shown that the principal compounds formed under different conditions are CO, CO_2, CH_3OH, AcOH, H_2O, and CH_3OOH with small amounts of HCOOH, CH_4, and C_2H_6.

It is noteworthy that compounds of the type RH are obtained only at low O_2 pressures (<1 mmHg) and, in order to suppress their formation, it is necessary to increase somewhat the oxygen pressure, raising simultaneously the temperature (for example, 0.0625 and 0.360 mmHg at 36° and 100 °C respectively).

Whereas the nature of the products formed is analogous to that of the compounds obtained in the thermal oxidation of acetone in the vapour phase at 280–320 °C, the relative compositions and kinetics of their formation are different and depend on the reaction time: in photochemical oxidation the amount of CH_3OH is much greater and OH is formed from the beginning of the reaction together with HCHO.

At a constant specified temperature the total amount of oxidation products increases with increase of the oxygen pressure (with the exception of CO, the amount of which decreases). It is of interest to note that more than 90% of the CO_2 is formed from the C=O group and CO is produced both from the CH_3 and C=O groups, the amount obtained from the latter group being smaller the higher the O_2 pressure; HCHO and CH_3OH are derived from CH_3 to an extent greater than 90%. Indeed, a study employing ^{14}C in the CH_3 group showed[61] that at 120 °C the amount of radioactive CO_2 is less than 10%. This result has been confirmed in studies[59,63] where the ^{18}O label was used over a wide temperature range, from 36° to 175 °C; the proportion of $^{16}O=C=^{18}O$ reached 92%. Furthermore, it has been shown[63] that proportion of $CH_3{}^{18}OH$ and $H_2C={}^{18}O$ is greater than 90%. In the first stage of the reaction acetone decomposes to methyl and acetyl radicals, this being followed by the partial decarbonylation of the latter, its extent increasing with increase of temperature and decreasing with increase of oxygen pressure:

$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3 \rightarrow H_3C^{\cdot} + {}^{\cdot}\overset{\overset{O}{\|}}{C}-CH_3 \ ;$$

$${}^{\cdot}\overset{\overset{O}{\|}}{C}-CH_3 \rightarrow CO + {}^{\cdot}CH_3 \ .$$

In the absence of O_2, two $H_3C^{\cdot}$ radicals recombine and a disproportionation reaction takes place between the $H_3C^{\cdot}$ and $O=\dot{C}-CH_3$ radicals, which leads to the formation of C_2H_6, CH_4, and $O=C=CH_2$ respectively:

$$H_3C^{\cdot} + {}^{\cdot}CH_3 \rightarrow H_3C-CH_3 \ ;$$

$$H_3C^{\cdot} + HCH_2-\overset{\overset{O}{\|}}{C}^{\cdot} \rightarrow CH_4 + H_2C=C=O \ .$$

In the presence of O_2 the radical $H_3C-\dot{C}=O$ gives rise to CO_2 and the radical $H_3CO^{\cdot}$, i.e.

$$H_3C-\overset{\overset{O}{\|}}{C}^{\cdot} \xrightarrow{O_2} H_3C-\overset{\overset{O}{\|}}{C}-O-O^{\cdot} \rightarrow {}^{\cdot}\overset{\overset{O}{\|}}{C}-O-OCH_3 \rightarrow CO_2 + {}^{\cdot}OCH_3 \ ,$$

while HCHO and the radical $^{\cdot}OH$ are formed from the radical $H_3C^{\cdot}$, i.e.

$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{}^{\cdot} \xrightarrow{O_2} H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-O-O^{\cdot} \rightarrow {}^{\cdot}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-O-OH \rightarrow \overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}=O + {}^{\cdot}OH$$

or H_2O and the radical $H-\dot{C}=O$ are produced:

$$\overset{\overset{H}{|}}{{}^{\cdot}\underset{\underset{H}{|}}{C}}-O-OH - H_2O + H-\overset{\overset{O}{\|}}{C}^{\cdot} \ .$$

The radicals $H_3C-C(=O)O^{\cdot}$ can be formed from the radicals $H_3C-\overset{\overset{O}{\|}}{C}-O-O^{\cdot}$:

$$H_3C-\overset{\overset{O}{\|}}{C}-O-O^{\cdot}$$

$$2H_3C-\overset{\overset{O}{\|}}{C}-O-O^{\cdot} \rightarrow 2H_3C-\overset{\overset{O}{\|}}{C}-O^{\cdot} + O_2 \ ,$$

while the radicals $H_3CO^{\cdot}$ can be formed from $H_3C-O-O^{\cdot}$:

$$2H_3CO-O^{\cdot} \rightarrow 2H_3CO^{\cdot} + O_2 \ .$$

The feasibility of the last reaction has been discussed in detail[66].

The products HCHO and H_3COH (the latter at least at the beginning of the reaction) are formed as a consequence of a disproportionation reaction between two methoxy-radicals:

$$H_3CO^{\cdot} + {}^{\cdot}OCH_3 \rightarrow H_3COH + HCHO \ .$$

This reaction has also been discussed[66].

Carbon monoxide can be formed via the two reactions presented below from the formyl radical obtained from the radical $H_2\dot{C}OOH$, the second reaction occurring at low oxygen pressures:

$$H-\overset{\overset{O}{\|}}{C}^{\cdot} + O_2 \rightarrow HO-O^{\cdot} + CO \ ;$$

$$H-\overset{\overset{O}{\|}}{C}^{\cdot} + H-\overset{\overset{O}{\|}}{C}^{\cdot} \rightarrow H-\overset{\overset{O}{\|}}{C}-H + CO \ .$$

The role of the reactions involving the abstraction of hydrogen by the radicals $H_3CO^{\cdot}$, $H_3CO-O^{\cdot}$, $H_3C-C(=O)-O^{\cdot}$, and $H_3C-C(=O)-O-O^{\cdot}$ increases with increasing temperature at least up to 200 °C. It is noteworthy that the abstraction of hydrogen from formaldehyde proceeds much more readily than from acetone. Indeed, depending on reaction time, the amount of HCHO passes through a maximum and the ratio $H_3COH/HCHO$ increases continuously; furthermore, when HCHO is introduced, the H_3COH content and the reaction rate increase. A new source of $H-\dot{C}=O$ radicals arises and hence the formation of CO is initiated.

At 250 °C the reactions involving the dehydrogenation of acetone by the above radicals become dominant and the rate of formation of all the compounds rapidly increases. The $H_3C-C(=O)CH_2$ radicals formed are oxidised to the corresponding peroxy-radicals, which become a new source of HCHO and the radicals $H_3C^{\cdot}$ as well as all their derivatives as a consequence of decomposition via the mechanism

$$H_3C-\underset{\underset{O}{\|}}{C}-CH_2O-O^{\cdot} \rightarrow HCHO + CO_2 + H_3C^{\cdot} \ .$$

The liquid-phase photochemical oxidation (λ = 313 nm) of acetone at 30 °C has been studied[64] and it has been shown that virtually the same reaction products are obtained as in the vapour phase at 284 °C. However, the amount of O_2 dissolved in acetone is insufficient for the complete suppression of the formation of CH_4 and C_2H_6, which suggests a greater ability of the $H_3C^{\cdot}$ radicals to abstract hydrogen and to dimerise in the liquid phase.

The photochemical oxidation of diethyl ketone at 25°, 100°, and 200 °C, diethyl ketone pressures of 35 or 12.5 mmHg, and oxygen pressures from 0 to 1.25 mmHg [67] and at 30°, 70°, 100°, and 150 °C, a diethyl ketone pressure of 35 mmHg, and oxygen pressures ranging from 0.55 to 1.85 mmHg [69] has been described[67-69]. These studies have been analysed in a review[22].

The principal reaction products include CO, CO_2, CH_3CHO, and C_2H_5COOH with small amounts of C_2H_4 and C_2H_6. Furthermore, it has been possible to establish by an isotope method that almost the entire amount of CO is formed from the carbonyl group (in contrast to acetone where the amount of CO derived from C=O does not exceed 20%) and that CO_2 at 30 °C is derived almost exclusively from C=O but at 100 °C only to the extent of 30%, while the remainder of the CO_2 arises from a group with a secondary carbon atom.

The above facts can be explained by the much easier decarbonylation of the radicals $C_2H_5\dot{C}=O$ than the radicals $H_3C\dot{C}=O$ and the much greater mobility of the hydrogen atom linked to a secondary carbon atom compared with a primary carbon atom (in the case of acetone). Consequently, for diethyl ketone all the hydrogen abstraction reactions are more important than in the oxidation of acetone. Hence it follows that the radicals $C_2H_5-\dot{C}=O$, $\dot{C}_2H_5$, and $C_2H_5-C(=O)-\dot{C}H-CH_3$ are formed even at room temperature in the initial stage of the reaction. The formation of different compounds can be represented by a sequence of steps:

$$C_2H_5-\underset{\underset{O}{\|}}{C}-C_2H_5 \xrightarrow{h\nu} C_2H_5-\underset{\underset{O}{\|}}{C}^{\cdot} + C_2H_5^{\cdot} \ ;$$

$$C_2H_5-\underset{\underset{O}{\|}}{C}^{\cdot} \rightarrow C_2H_5^{\cdot} + CO \ ;$$

$$C_2H_5^{\cdot} + C_2H_5-\underset{\underset{O}{\|}}{C}-CH_2-CH_3 \rightarrow C_2H_6 + C_2H_5-\underset{\underset{O}{\|}}{C}-\dot{C}H-CH_3 \ ;$$

$$C_2H_5-\underset{\underset{O}{\|}}{C}-\dot{C}H-CH_3 \rightarrow C_2H_5-\underset{\underset{O}{\|}}{C} + H_2C=CH_2 \ ;$$

$$C_2H_5-\underset{\underset{O}{\|}}{C}^{\cdot} \xrightarrow{O_2} C_2H_5-\underset{\underset{O}{\|}}{C}-O-O^{\cdot} \rightarrow CO_2 + {}^{\cdot}OC_2H_5 \ ;$$

$$H_3C-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-O-O^{\cdot} \rightarrow H_3C-\overset{\overset{H}{|}}{C}=O + {}^{\cdot}OH \ ;$$

$$C_2H_5-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{O}{\|}}{C}^{\cdot} \xrightarrow{O_2} C_2H_5-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{O}{\|}}{C}-O-O^{\cdot} \rightarrow \underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-O-O + C-C_2H_5 \ ;$$

$$\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-O-\underset{\underset{O}{\|}}{C}-C_2H_5 \rightarrow \overset{\overset{H}{|}}{C}=O + {}^{\cdot}O-\underset{\underset{O}{\|}}{C}-C_2H_5 \ ;$$

$$C_2H_5-\underset{\underset{O}{\|}}{C}-O^{\cdot} + C_2H_5-\underset{\underset{O}{\|}}{C}-CH_2-CH_3 \rightarrow C_2H_5-\underset{\underset{O}{\|}}{C}-OH + C_2H_5-\underset{\underset{O}{\|}}{C}-{}^{\cdot}CH-CH_3 \ ;$$

$$H_3C-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{C}} + R^{\cdot} \rightarrow H_3C-\underset{\underset{O}{\|}}{C}^{\cdot} + RH \quad (R = C_2H_5^{\cdot},\ C_2H_5-\underset{\underset{O}{\|}}{C}^{\cdot}) \ ;$$

$$H_3C-\underset{\underset{O}{\|}}{C}^{\cdot} \xrightarrow{O_2} H_3C-\underset{\underset{O}{\|}}{C}-O-O^{\cdot} \rightarrow CO_2 + {}^{\cdot}OCH_3 \ .$$

The reaction involving the abstraction of a hydrogen atom from H_3C-CHO is analogous to the abstraction of hydrogen from HCHO in the case of acetone. In the absence of oxygen, C_2H_6 and C_2H_4 are mainly formed[70].

The thermal oxidation of dipropyl ketone has been studied[35] and it has been shown that the maximum concentration of the hydroperoxide is 0.005 and 0.010 mole per mole of the initial substance at 110° and 120 °C respectively; these concentrations are reached after 24 and 5 h respectively. Under the same conditions, the concentrations of acids are 0.03 and 0.04 mol mol^{-1} and reach 0.05 and 0.08 mol mol^{-1} after 30 h at 100 °C and after 12 h at 120 °C.

The thermal oxidation of di-isopropyl ketone has been investigated[36] at 100° and 110 °C; the maximum content of the hydroperoxide reaches 0.05 and 0.04 mole per mole of the initial substance at 100° and 110 °C after 36 and 16 h respectively.

The oxidation of di-isopropyl ketone in a highly alkaline medium has been studied[46,49]. In the presence of $(CH_3)_3COK$ in a $(CH_3)_3COH$ + diglyme mixture the conversion of the ketone is complete after 45 h, the yield of the hydroperoxide amounting to 0.8 mol mol^{-1}.[49] The same alkoxide in solution in dimethyl formamide at −8 °C reacts completely after 4 min and the yield of the hydroperoxide is 0.87 mol mol^{-1}. Cubbon and Hewlett[46] studied the structure of the hydroperoxide

$$(CH_3)_2C(OOH)-CO-CH(CH_3)_2 \qquad \text{(IV)}$$

obtained by thermal oxidation at 100 °C as described by Scarp and Whitcome[36] or by base-catalysed oxidation at −8 °C as described by Gersmann and Bickel[48]. The absence of a cyclic structure of the type

$$(CH_3)_2\overset{\overset{OH}{|}}{C}(O-O)-CH(CH_3)_2$$

was demonstrated by the retention of specific properties of the O–OH and C=O groups. Indeed, in the presence of phenylhydrazine it is possible to obtain the hydroperoxide

$$(CH_3)_2C(OOH)-\underset{\underset{N-NHC_6H_5}{\|}}{C}H(CH_3)_2$$

and in the presence of $(C_6H_5)_3CCl$ the dialkyl peroxide

$$(CH_3)_2C(O-O-C(C_6H_5)_3)-COCH(CH_3)_2$$

can be synthesised.

The presence of a single hydroperoxy-group (with intramolecular and intermolecular hydrogen bonds) in the reaction product is fairly unexpected, because the simultaneous presence of two tertiary carbon atoms creates favourable conditions for attack at two positions simultaneously. The hydroperoxide decomposes via a radical mechanism (initiation of the polymerisation of vinyl monomers).

The oxidation of 2-octanone[42] at 130 °C and 15 atm in an alkaline medium in the presence of NaOH (from 0 to 4.25 *N*) has been studied[42] and it has been shown that, apart from the main attack on the 3-position (relative to the end of the chain), leading to the formation of C_2 and C_6 monobasic acids, there is attack on other positions albeit to a lesser extent. It is of interest to note that the direction of this attack varies with the alkalinity of the medium; with increase of alkalinity, the CH_2 group is involved to a lesser extent but the interaction with the CH_3 group in the α-position relative to C=O intensifies.

Thus in a neutral medium the overall yield of the C_2 and C_6 acids is 77% and the yield of α-oxoheptanoic acid is 2% of the overall yield of all the acids, while in an alkaline medium (NaOH, 6.25 *N*) the yields of the C_2 and C_6 acids are 63 and 18% respectively. On passing from a neutral to an alkaline medium, the yields of the C_3 and C_4 acids diminish somewhat, from 6.2 to 4.4% and from 8.4 to 6.5% respectively.

The thermal oxidation of γ-undecanone at 140 °C has been studied[43] under a pressure of 15 atm. As in the previous case, oxygen acts not only on the carbon atom in the 5-position relative to the end of the chain but also on all the carbon atoms although to a much smaller extent; this gives rise to the formation of both C_5 and C_6 acids, on the one hand, and of C_2, C_3, and C_4 acids, γ-oxovaleric acid, and β- and γ-oxocapric acids, on the other, as well as the formation of diketones (3,6- and 2,6-undecanediones) and methylethylbutyrolactone. The preferential attack on the 2-position (the α-position relative to the CH_3 group) is noteworthy. The amounts of the C_2, C_3, C_4, and C_5 acids formed relative to the C_6 acid are 0.17, 0.11, 0.10, and 0.66 respectively.

The amount of peroxides passes through a sharp maximum (8×10^{-2} mol mol^{-1}), which is attained after 20 min; after 2.5 h, the products contained 5×10^{-2} mol mol^{-1} of peroxides, 5×10^{-2} mol mol^{-1} of esters (after 3 h), and 1×10^{-2} mol mol^{-1} of lactones (after 3 h).

Esters can be formed partly as a result of the reaction with the initial ketone of the peroxide formed by the oxidation of the aldehydes formed. This is the classical Baeyer–Villiger reaction described by Hassall[71] and the present author[72].

The thermal oxidation of γ-undecanone has also been studied at 120° and 130 °C;[43] the maximum content of different compounds in the product is almost independent of temperature but is attained faster at higher temperatures. Thus the maximum amounts of products are formed after 180, 90, and 30 min for peroxides (8×10^{-2} mole), after 300, 180, and 90 min for acids (6×10^{-2} mole), and after 360, 180, and 150 min for esters (3×10^{-2} mole) at 120°, 130°, and 140 °C respectively.

It has been established[73] that benzyl mesityl ketone is converted at room temperatures into mesiteic acid and benzaldehyde on contact with even traces of atmospheric oxygen. The yield of the intermediate hydroperoxide $C_6H_5-CH(O-H)-COMes$ is 0.07–0.08 mol mol^{-1} and is reached after a period ranging from 15 days to 6 months. The hydroperoxide isolated in a pure form is a crystalline substance which melts with decomposition at 134–135 °C. After reduction by treatment with KI or Na_2SO_3 in acetic acid, the corresponding ketoalcohol is obtained, while heating up to 100–110 °C at a pressure of 1 mmHg results mainly in the formation of mesiteic acid, benzophenone, and a small amount of dibenzoyl and water.

IV. SYNTHESIS AND STUDY OF THE DECOMPOSITION OF α-KETOHYDROPEROXIDES

1. Synthesis

Hydroperoxides of different types, presented in Tables 2 and 3, have been obtained[74] by oxidising aldehydes or ketones ketones in an alkaline medium at −20 °C in the presence of $(CH_3)_3COK$ in $(CH_3)_3COH$ (method I) or C_2H_5ONa in C_2H_5OH + DMF (method II) with subsequent recrystallisation of the reaction products from an appropriate solvent.

Table 2. Hydroperoxides of the type $XC_6H_4-C(=O)-C(O-OH)(C_6H_5)-C_6H_5$.

X	Method	Solvent for recrystallisation	Purity, %	M.p., °C
H	I	petroleum ether	96	115—116
H_3CO-*p*	II	hexane + petroleum ether	85	118—119
H_3C-*p*	II	benzene + petroleum ether	77	112—114
Cl-*m*	II	benzene + petroleum ether	88	101—103
Cl-*m*	II	—	67	liquid

Table 3. Hydroperoxides of the type $C_6H_5-C(=O)-C(O-OH)(C_6H_5)-CH_2C_6H_4X$-*p* obtained by method II.

X	Solvent of recrystallisation	Purity, %	M.p., °C
CH_3O	benzene + petroleum ether	29	105—108
H_3C	—	50	liquid
Cl	—	60	liquid

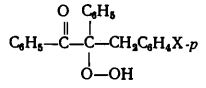
2. Various α-Ketohydroperoxide Decomposition Pathways

Various methods for the thermal[74] (at 250 °C in the vapour phase or at 130 °C in the liquid phase in chlorobenzene), photochemical[75], and alkali-catalysed[76] decomposition of α-ketohydroperoxides have been studied in very great detail. The papers indicated present the ratios of products in each individual instance and discuss the relevant mechanisms.

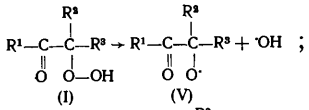
(a) The radical mechanism. The thermal decomposition of α-ketohydroperoxides in the vapour phase at 250 °C or in the liquid phase at 130° and 150 °C in C_6H_5Cl as well as their photochemical decomposition at room temperature give rise to the acid R^1COOH and the ketone R^2COR^3 as the main products

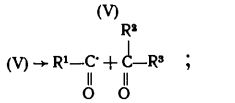
in yields of 0.75–0.80 and 0.75–1.00 mole per mole of the initial substance respectively. These products are formed as a result of the rupture of the bond between the carbon atom of the carbonyl group and the carbon atom linked to the hydroperoxy-group. Small amounts of R^1COCOR^2, the alcohol R^3OH, and the hydrocarbon R^3R^3 are also formed as a result of the dissociation of the C–C bond in the β-position relative to the C=O group. The ease of dissociation depends on the nature of R^3.

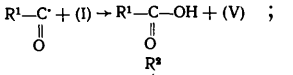
In the case of hydroperoxides

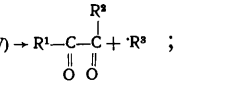


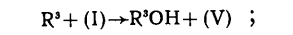
the yield of $C_6H_5-C(=O)-C(=O)-C_6H_5$ is 0.04, 0.054, and 0.08 mole per mole of the initial substance for X = Cl, H, and OCH_3 respectively. Consequently electron-accepting groups lower and electron-donating groups increase the rate of dissociation of the C–C bond in the β-position. The increased yield of the acid R^1COOH or the ketone R^2COR^3 as well as the fact that the rate of reaction in C_6H_5Cl is higher than in other solvents suggest that the thermal decomposition proceeds via a radical mechanism including a sequence of steps:

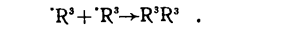

(1)


(2)


(3)

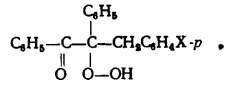

(4)


(5)


(6)

The first stage is the homolytic dissociation of the oxygen bridge in compound (I) with formation of radicals (V) and ·OH; this is followed by reactions (2)–(6). The main reactions are (2) and (3) and the side reactions are (4), (5), and (6). The contribution of the ionic mechanism under the experimental conditions given above (dilution to a low concentration in a non-polar solvent) is apparently insignificant. Furthermore, since the yields are analogous to those quoted in the previous instance (for the formation of the acid R^1COOH and the ketone R^2COR^3 in the photochemical decomposition of the above hydroperoxides at room temperature), presumably this process also involves a radical chain mechanism[75].

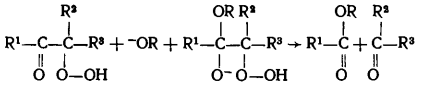
It is noteworthy that the oxidation-reduction reaction at 25 °C in aqueous 70% CH_3OH solution in the presence of $FeSO_4$ also proceeds via a radical mechanism analogous to that described by Sawaki and Ogata[74]. The hypothesis of the formation of the radicals $R^1\dot{C}O$ is also supported by the formation of the diketone R^1COCOR^1 in a yield of ~0.17–0.20 mol mol^{-1} for hydroperoxides of the type



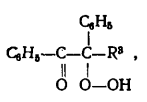
In contrast to cumenyl hydroperoxide, the α-ketohydroperoxide is not reduced to the corresponding alcohol. In the simultaneous presence of $FeSO_4$ and $FeCl_3$, R^1COOCH_3, $R^2R^3C=O$, and R^3Cl are formed in amounts of 0.4–0.6, 0.5–1.0 and 0.018–0.013 mole per mole of the initial substance respectively.

Kochi and Rust[77] discussed in detail the recombination of radicals in the presence of metal ions, while de la Mare and Kochi[78] published a similar discussion of the reduction and oxidation by metal salts.

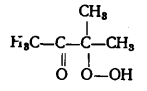
(b) Ionic decomposition catalysed by strong acids. This procedure has been studied in detail by Sawaki and Ogata[76]. It was shown that, in the presence of alkaline alkoxides ROM, where M = K or Na, in the corresponding alcohol or in an alcohol with added benzene at temperatures ranging from 0 °C to room temperature, the ester R^1COOR is formed almost exclusively with a small amount of the acid R^1COOH; however, the content of the latter increases with decrease of the ROM concentration and with increase of the amount of H_2O. Kinetic data suggest that the first reaction stage is the addition of the ^-OR anion to the carbonyl group followed by the heterolytic dissociation of the oxygen bridge and the C–C bond in the anion formed:



The rate of reaction evaluated from the amount of decomposed hydroperoxide varies very markedly with the structure of the hydroperoxide and also with the nature of the group linked to the C=O group compared with that linked to the COOH group. Thus for a hydroperoxide of the type



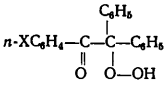
where R^3 = C_6H_5, CH_3, C_2H_5, or $C_6H_5CH_2$ (under the following identical conditions: temperature 0 °C, CH_3ONa concentration 0.10 M in a 1 : 1 mixture of CH_3OH and C_6H_6), the rates of decomposition (in relative units) are 308, 10.5, and 4.9 (the rate of decomposition of the hydroperoxide



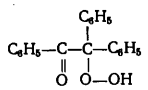
was adopted as unity). The replacement of the C_6H_5 group by C_2H_5 lowers the rate of decomposition by a factor of 30 and the replacement by $C_6H_5-CH_2$ lowers it by a factor of 60; the yield of the ketone R^2COR^3 decreases in the same sequence: from 0.98 for R^3 = C_6H_5 to 0.77 mole per mole of the initial substance for R^3 = $C_6H_5CH_2$.

It is noteworthy that the relative rate of decomposition of the hydroperoxide $(CH_3)_2CH-\underset{\underset{O}{\|}}{C}-\underset{\underset{O-OH}{|}}{C}(CH_3)_2$ is 0.078, diminishing by a factor greater than 13 on replacement of the CH_3 group by $(CH_3)_2CH$.

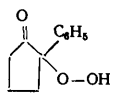
When the rate of decomposition for X = H is adopted as unity, the relative rates corresponding to X = CH_3O, CH_3, and Cl for hydroperoxides of the type



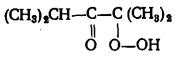
(the conditions were the same as above but CH_3ONa was replaced by C_2H_5ONa) are 0.11, 0.33, and 4.8, the rate diminishing by a factor of 14 following the replacement of the C_6H_5 group (linked to C=O) by CH_3 in



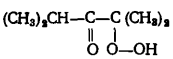
An especially high rate of decomposition of the hydroperoxide



has been noted. It is 7550 times greater than for the hydroperoxide

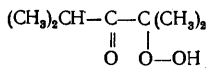


The above results depend mainly on the difference between the rates of addition of the anion ^-OR to the group C=O, caused by polar and particularly steric factors. Thus the rate of decomposition of the hydroperoxide

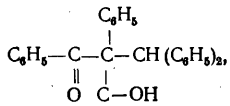


is extremely low due to steric hindrance. The rate of decomposition also varies with the RONa concentration: it increases by a factor of 4.5 for the $C_2H_5ONa/(CH_3COH + C_6H_6)$ system at 0 °C when the RONa concentration is raised by a factor of 20 (from 5×10^{-3} to 10^{-1} M) and increases by a factor of 25 with increase of temperature to 25 °C.

It is noteworthy that the ketone R^2COR^3 has been obtained in a yield of 0.8 mol mol^{-1} in a study[79] of the decomposition of the hydroperoxides

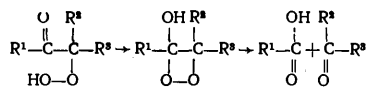


and



also in an alkaline medium but under other conditions (30 °C, $NaOH/CH_3OH + H_2O$ at a concentration of 0.1–0.5 M or CH_3ONa/CH_3OH at a concentration of 5×10^{-2}–5×10^{-1} M). Another compound formed was mainly the acid R^1COOH; the ester R^1COOCH_3 was obtained only in a yield of 0.13–0.16 mole per mole of the initial substance.

The results described suggest that the competitive addition of the groups RO^- and ^-OH to the carbonyl group leads to the formation of an ester and an acid. Furthermore, on the basis of kinetic data and luminescence phenomena, observed in the course of the decomposition of the hydroperoxides investigated, the authors[79] suggested that, as a consequence of the addition of the hydroperoxide hydrogen to the carbonyl group, a dioxetan is formed as an intermediate:



v. OXIDATION REACTIONS OF ALICYCLIC KETONES

1. Monocyclic Ketones

Three types of methods have been used to investigate monocyclic ketones, in particular cyclohexanone and its methyl derivatives:

(a) oxidation in a neutral medium at 100 °C of a purely thermal type or in the presence of catalysts based on variable-valence metal salts;

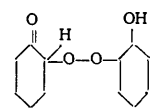
(b) oxidation in an acid medium at 60–70 °C;

(c) oxidation in a highly alkaline medium below room temperature.

In the first two cases the reaction products consist mainly of dicarboxylic acids (or their derivatives) formed as a result of ring rupture; in the third case the products are α-diketones (without ring dissociation), which are obtained by the dehydration of the intermediate hydroperoxides or from the products of their subsequent condensation.

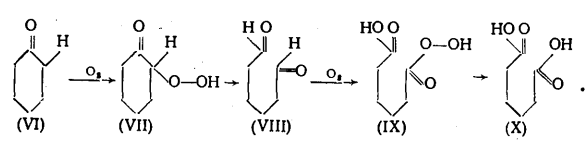
It has been shown[37] that the rate of oxidation of cyclohexanone in a neutral medium at 76 °C is low, becoming considerable at 100 °C. The kinetics of the formation of peroxides at 110°, 120°, and 130 °C have been determined by Denisov and Denisova[80]. Pritzkow[38] carried out the oxidation at 100 °C in the absence and presence of manganese laurate and determined the compounds obtained as well as the kinetics of the formation of peroxides and acids. It is noteworthy that in the presence of manganese laurate the maximum content of hydroperoxide is 9×10^{-3} mole per mole of the initial substance and is attained after only 2 h from the start of the reaction and the corresponding overall amount of the acids is 4.6×10^{-1} mole per mole of the initial substance, i.e. 7 times greater than in the absence of the catalyst.

By concentrating the crude oxidation product at a reduced pressure, it was possible[38] to obtain a product containing 10^{-1} mol mol^{-1} of peroxides. It decomposes 80 times faster in cyclohexanone than in cyclohexane, which suggests that cyclohexanone is involved in the formation of radical chains via the formation of the intermediate hydroperoxide



obtained as a consequence of the intermolecular addition of the hydroperoxide hydrogen to the carbonyl group[80]. The same phenomenon has been observed also in the general case where carbon compounds are treated with hydroperoxides[23].

The compounds obtained consist mainly of C_4, C_5, and C_6 dicarboxylic acids, with adipic acid predominating, and of smaller amounts of C_5 and C_6 monobasic acids; ω-hydroxycaproic acid and the corresponding lactone are also formed. Adipic acid is formed via a radical mechanism (probably a chain mechanism), which can be represented by the following simplified scheme:



(VI) (VII) (VIII) (IX) (X)

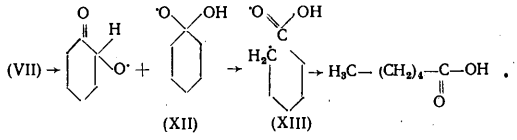
The C_5 dicarboxylic acid is formed as a result of the decarboxylation of the peracid (IX) with formation of radicals (XI) and $^{\cdot}OH$, the former being oxidised to the corresponding

semialdehyde via the classical mechanism

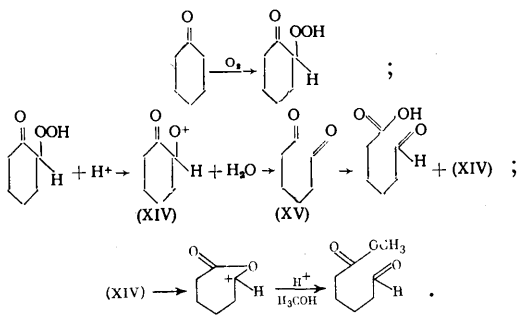
$$(IX) \rightarrow CO_2 + {}^{\cdot}OH + HO{-}CO(CH_2)_3{-}CH_2^{\cdot};$$

$$(XI) + O_2 \rightarrow HO{-}CO(CH_2)_3{-}CHO + {}^{\cdot}OH\ .$$

Monobasic acids may be formed from the hydroperoxide (VII) via the homolytic dissociation of the peroxy-bridge with subsequent dissociation of the carbon–carbon bond and the elimination of hydrogen:



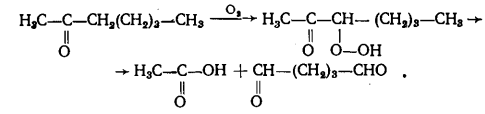
The oxidation process in an acid medium has been investigated[81] at 60 °C in CH_3OH in the presence of 4% H_2SO_4 relative to the ketone. As for the oxidation in a neutral medium, the main products (0.70 mole per mole of the initial substance) are formed via the ring dissociation; they consist of derivatives of adipic semialdehyde (0.45 mole), its oxidation product—adipic acid (0.15 mole), and ω-hydroxycaproic acid (0.10 mole). The acid group is bound in the form of the methyl ester and the aldehyde group is bound in the form of the dimethyl acetal. These compounds are formed in the presence of acids via an ionic mechanism:



Oxidation in an alkaline medium has been investigated[82] in the $(H_3C)_3COK{-}(CH_3)_3COH{-}$diglyme system. It was shown that at −20 °C the degree of dissociation of the ring is low and that the main product (0.6 mol mol^{-1}) is α-cyclohexanedione, adipic acid being formed in the smallest amount (0.1 mol mol^{-1}). Only tarry products are obtained at room temperature in the presence of CH_3ONa/CH_3OH,[83] but in hexamethylphosphoramide (HMP) solution in the presence of NaOH or CH_3ONa adipic acid is formed in a yield of 0.80 mol mol^{-1} at 24° or 80 °C.[84]

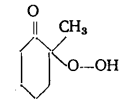
The oxidation of 2-methylcyclohexanone has been investigated in a neutral medium[85] at 100 °C in the presence of $(1–5) \times 10^{-4}$ mol mol^{-1} of copper stearate. The main products are α-ketohydroperoxide, ε-methylcaprolactone, and oxoheptanoic, caproic, and acetic acids with a small amount of methyladipic, glutaric, succinic, methylsuccinic, and $C_3–C_6$ monocarboxylic acids. Compared with the non-catalytic oxidation, the catalyst apparently drives the reaction towards the formation of acids and the amount of the latter depends little on its concentration.

The nature of the compounds obtained suggests that the main attack is directed to the carbon atom in the α-position (with the CH_3 group); this results in the formation of a tertiary hydroperoxide, which then decomposes via a radical mechanism to 6-oxoheptanoic acid. Using the reoxidation method, the latter can be used as a source of monobasic acids, namely acetic acid:



However, the formation of α-methyladipic acid indicates the attack of O_2 on the α-position relative to the secondary carbon atom.

The oxidation of 2-methylcyclohexanone has been investigated[46] in the presence of NaOH or CH_3ONa in dimethylformamide as the solvent. At −50 °C the hydroperoxide



can be isolated in the form of a liquid; at −10 °C the main reaction product is oxoheptanoic acid.

The oxidation of 3-methylcyclohexanone in the presence of cobalt stearate at concentrations from 5×10^{-4} to 5×10^{-2} mol mol^{-1} has been studied by Serov et al.[86] The main products consist of α-methyladipic, δ-oxocaproic, and acetic acids; the secondary compounds are dicarboxylic acids; β-methyladipic, α-methylglutaric, and methylsuccinic acids. The results confirm the hypothesis that oxygen attacks the two secondary carbon atoms in the α- and α′-positions relative to the C=O group and the tertiary carbon atom. The quantitative composition of the products and hence the intensity of the attack on these positions are influenced by the temperature, the reaction time, and concentration.

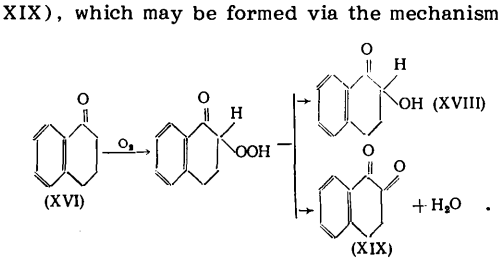
The thermal oxidation of methylcyclohexanone isomers has been investigated in detail[87] in the presence of cobalt(II) and manganese(II) stearates and cobalt(III) and manganese(II) acetylacetonates as catalysts.

Rao et al.[82] described the oxidation of $C_5–C_8$ cyclanones in the highly alkaline $(CH_3)_3COK{-}(CH_3)_3COH{-}$diglyme medium at −20 °C. It was observed that 1,2-cyclopentanedione and glutaric acids are formed from cyclopentanone in yields of 0.36 and 0.19 mole per mole of the initial substance respectively, while α-diones are obtained from the C_7 and C_8 cyclanones and then undergo aldolisation with formation of spiran derivatives[82].

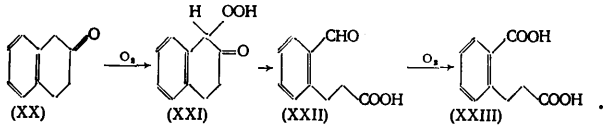
This difference in behaviour as a function of the type of ring can be due to the fact that the C_5 and C_6 diones almost always exist in the enolic form, which prevents the aldolisation reaction, while the C_7 and C_8 cyclanones exist in the keto-form and readily undergo this reaction[82].

2. Cyclanones with Condensed Rings

The thermal oxidation of α- and β-tetralinones in a neutral medium has been studied[37]. The products obtained from the α-isomer (XVI) consist of peroxides [most probably largely of the hydroperoxide (XVII)], naphthoquinol (XVIII), and the diene (XIX), which may be formed via the mechanism



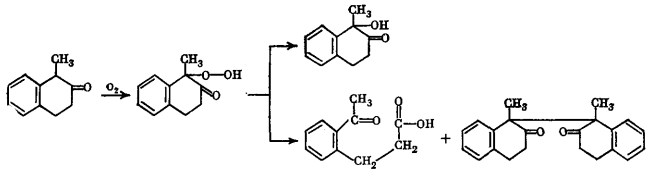
In the case of the β-isomer a single product was isolated—*o*-carboxyphenylpropionic acid (XXIII), which is apparently formed via an intermediate hydroperoxide (XXI):



(XX) (XXI) (XXII) (XXIII)

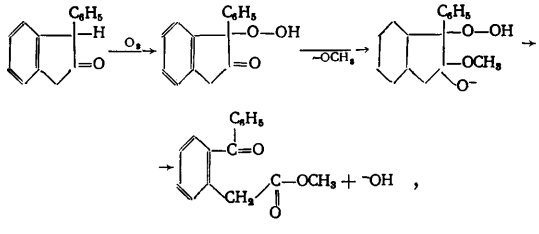
It is noteworthy that the rate of oxidation of the β-isomer is much higher than that of the α-isomer, because the carbon of the methylene group is located between the C=O and C_6H_5 groups.

The oxidation of α-methyl-β-tetralinone at room temperature has been studied by Naispuri et al.[88] The composition of the products formed via the mechanism



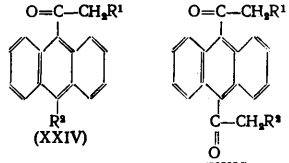
is as follows: 2-acetylphenylpropionic acid (main product, yield 0.3 mol mol^{-1}); 3,4-dihydro-1-hydroxynaphthalin-2(14)-one; 1,1-bis-3,4-dihydro-1-methylnaphthalin-2(14)-one. The latter is obtained as a result of the dimerisation of the initial keto-radical. It was not possible to isolate the hydroperoxide in a pure form.

The oxidation of 1-phenyl-2-indanone has been studied[89] in an alkaline medium (CH_3ONa/CH_3OH), and methyl *o*-benzoylphenylacetate, probably formed via the mechanism of Sawaki and Ogata[76], which in the given instance reduces to the mechanism



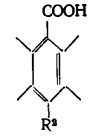
was obtained.

The oxidation (in an alkaline KOH/CH_3OH medium at room temperature) of α-monoketones and several anthracene α,α'-diketones having the general formula



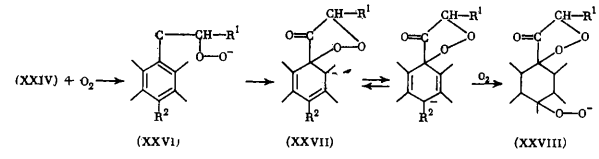
(XXIV) (XXV)

has been the subject of an interesting study by Rao et al.[90] In contrast to the classical mechanism, the products do not consist of the acid



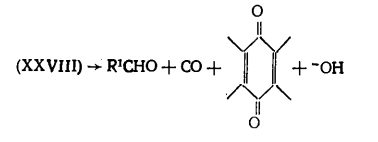
and the aldehyde R^1CHO; their nature depends on the substituent R^2. Thus anthraquinone is formed for R^2 = H and hydroxyanthrone is formed for $R^2 = C_6H_5$; in addition CO is produced in both instances.

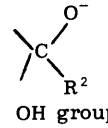
The formation of the above compounds can be accounted for by the following mechanism: the peroxide anion formed in the initial stage adds to the nearest carbon atom in the *meso*-position to form a five-membered ring, which causes the migration of the double bond and the appearance of a negative charge on another carbon atom in the *meso*-position, which is in its turn oxidised:

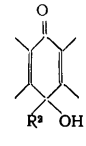


(XXVI) (XXVII) (XXVIII)

The course of the decomposition of compound (XXVIII) depends on the nature of R^2: the following reaction takes place when R^2 = H:

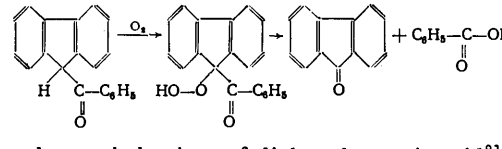


When $R^2 = C_6H_5$, the $>C-O-O-$ groups are reduced to  (probably by the initial ketone) with formation of the OH group, which is followed by the formation of hydroxyanthrone:



The oxidation of fluorenyl phenyl ketone in an alkaline medium has been described[91]. In a neutral or weakly alkaline medium ($NaHCO_3$) at pH 8.4 oxygen is not absorbed and at pH 12 the absorption is very slow; it is significantly accelerated in a highly alkaline medium, for example in $KOH-C_2H_5OH-H_2O$, and the yield of fluorenone becomes 0.85 mol mol^{-1}.

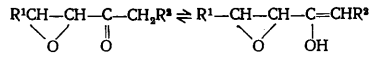
Fluorenone is formed by a general mechanism via the α-ketohydroperoxide:



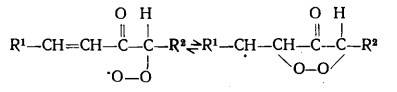
The analogous behaviour of diphenylpyruvic acid[91]—oxidation with formation of oxalic acid and benzophenone—is noteworthy. The intermediate hydroperoxide could never be isolated because of its instability.

VI. OXIDATION OF α,β-UNSATURATED KETONES

The oxidation of ketones of this type has been studied mainly in an alkaline medium (KOH/CH_3OH) above room temperature. In all cases the main reaction is the formation of an epoxyketone, which is in equilibrium with the corresponding unsaturated ketol:



This can be followed by hydrolytic oxidative dissociation steps with formation of various compounds. Hydrogen peroxide, formed by the hydrolysis of the allyl hydroperoxide produced initially, can serve as the epoxidising agent. It is noteworthy that attack by oxygen is more likely to be directed to the carbon atom located in the α-position relative to the double bond than to the carbon atom in the α-position relative to the C=O group. Indeed the peroxy-radical arising in the second case should have been stabilised, by virtue of its resonance structure, by addition to a double bond with formation of a five-membered ring:



Incidentally, it is known that α,β-unsaturated aldehydes are oxidised with much greater difficulty than the corresponding saturated aldehydes[8,10].

The oxidation of mesityl oxide[24], pent-3-en-2-one,[92] pulegone[93], piperitone[94,95], carvenone[96], carvone[97], 1-methylcyclohex-1,2-en-3-one, 1,5-dimethylcyclohex-1-en-3-one, verbenone, carvotanacetone, isophorone, and eucarvone[98] has been investigated.

VII. INTERACTION OF STEROID KETONES WITH OXYGEN

The oxidation of various steroid ketones in an alkaline medium has been considered by comparison with certain simple ketones[99] and examples of compounds formed depending on the nature of the initial ketone, have been given.

The studies of Bailey et al.[100] and of Gardner et al.[101] were concerned with the hydroxylation of pregnan-20-ones to the corresponding hydroxy-compounds. In principle, the process consists in the oxidation of the ketone in an alkaline medium (CH_3ONa/CH_3OH + DMF) with reduction of the α-ketohydroperoxide *in situ* to the corresponding ketoalcohol. The reducing agent can be H_2 [100] or $P(CH_3O)_3$.[101] The latter reduction method is more effective, because the yield of the ketoalcohol reaches 65%. This reaction has been discussed in detail by Gardner et al.[101]

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Chemical and Biological Kinetics

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Examples of the application of the methods and ideas of chemical kinetics in various branches of chemistry and biology are considered and the results of studies on the kinetics and mechanisms of atuoxidation and inhibited and catalysed oxidation of organic substances in the liquid phase are surveyed. Problems of the kinetics of the ageing of polymers and the principles of their stabilisation are discussed and certain trends in biological kinetics (kinetics of tumour growth, kinetic criteria of the effectiveness of chemotherapy, problems of gerontology, etc.) are considered.
The bibliography includes 281 references.

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I. INTRODUCTION

Approximately half a century ago a new branch of natural science began to be formulated in various countries, namely chemical physics, which deals with the physical principles of chemistry and includes the physics of the structure of matter and of chemical reactions (chemical kinetics).

In 1931 Academician N.N.Semenov founded in the USSR the Institute of Chemical Physics of the USSR Academy of Sciences which has since celebrated its 50th anniversary. In this Institute, which has a long tradition in the field of kinetic research, general kinetics have been developed in many directions. At the time of the organisation of the Institute the studies of a group of scientists working under Semenov's supervision at the Physicotechnical Institute in Leningrad led to the discovery of branched chain reactions and laid the foundations of the theory of chain inflammation and thermal explosion. These scientific advances rapidly received high recognition in world science. They have occupied an important place as the foundation of Soviet chemical physics, which is distinguished by specific research into the kinetics and mechanisms of chemical reactions and combustion and explosive processes.

A quantitatively rigorous general theory of chemical chain reactions was created. This theory deals with the quantitative aspects of unbranched chain processes which have become the object of studies in chemical kinetics at the beginning of this century as a result of the outstanding research of Bodenstein and Nernst. The theory of chain termination on walls and within the space of the reaction vessel has been developed in the Institute of Chemical Physics of the USSR Academy of Sciences for unbranched chain reactions and the general case of chain termination in space and on the surface has been considered theoretically. Differential equations and their integral forms, whereby chain propagation can be described as a function of time, i.e. the

kinetics of chain reactions can be described, have been obtained. A theory of branched chain processes has been particularly thoroughly developed for the case of chain branching as a result of the multiplication of active centres (atoms and radicals) in the chemical interaction of active centres with molecules as well as a theory of energetic chain branching due to the excess energy of the reaction products (in the 1960's). Many new phenomena characteristic of branched chain processes have received a clear physical interpretation and a theoretical foundation. These are in the first place a theory of the lower and upper inflammation limits and the discovery of an unusual form of the regions of the chain inflammation of combustible gases in the form of "peninsulas" in terms of pressure–temperature variables.

A theory of degenerate branched chain reactions has been created. This theory made it possible to understand and describe quantitatively many instances of the slow development of a chain avalanche which does not lead to the inflammation of the combustible gas mixture. Subsequently many slow oxidation reactions of organic substances, initially in the gas phase and then in a condensed phase (in the liquid state and in solid polymers) were examined from the standpoint of this theory.

Much attention has been devoted to the study of the detailed chemical mechanisms of chain reactions, the identification of free atoms and radicals, the determination of their concentrations, and the study of elementary processes involving them.

The Institute of Chemical Physics has made a fundamental contribution to the theory of combustion and explosive processes, the thermal explosion of gases and condensed explosives, the propagation of flame in connection with the kinetics of chemical combustion reactions, and the detonation theory.

The mathematical apparatus of general kinetics consist of systems of differential kinetic equations including time as an independent variable.

A system of the type

$$\frac{dF_i}{dt} = f_i(F_1, F_2, \ldots F_n; t; a_1, a_2, \ldots a_m)$$

taking into account, when necessary, also heat and mass transfer, makes it possible to describe the kinetics of a wide variety of processes in chemistry, physics, biology, and geology. In this equation F_i are quantities varying with time and characterising the properties of the system, t is the time, and a_1, a_2, ..., a_m is a set of constant parameters. If the equations can be integrated in terms of quadratures, a set of formulae is obtained for the description of the kinetic curves for the process under consideration:

$$F_i(t) = \int_{t_0}^{t} \frac{dF_i}{dt} dt \quad .$$

The laws governing the development of gas-phase reactions represent the most complete field of general kinetics. Despite their enormous theoretical and practical importance, the kinetics of chemical reactions in condensed systems (liquid and solid) have been less thoroughly developed. The kinetics of biological processes have been still less developed.

This review is devoted to the kinetics of liquid-phase reactions in relation to the oxidation of organic substances, the chemical physics of the ageing and stabilisation of polymers, and the kinetics of certain biological processes.

II. KINETICS OF THE LIQUID-PHASE OXIDATION REACTIONS OF ORGANIC SUBSTANCES

During the last quarter of the century, considerable progress has been achieved in the kinetics and mechanisms of the oxidation processes of organic substances in the liquid phase.

1. Chemical Oxidation Mechanism

As a result of numerous studies throughout the world, the fundamental oxidation mechanism has been established. It includes elementary stages involving chain initiation (the formation of primary free radicals), chain propagation—the so-called "degenerate" branching, which lags behind the time of propagation of the main chain, the molecular decomposition of the peroxide with formation of a wide variety of oxidation products, and chain termination, which consists as a rule in the recombination of the radicals $R\dot{O}_2$.

The oxidation reaction does not always occur in an "unperturbed" form of this kind. In many instances the oxidation takes place in the presence of various inhibitors and catalysts, so that the overall oxidation mechanism is significantly complicated. In the general case account must be taken of the reactions of the active radicals $R\dot{O}_2$ and $\dot{R}$ as well as hydroperoxides with inhibitors and their reaction products, the set of elementary processes occurring in the presence of more than one inhibitor in the system, the complex formation reactions of homogeneous and heterogeneous catalysts with virtually all the starting materials, intermediates, and final products, and the reactions of the resulting complexes.

Thus the oxidation mechanism can be represented by the following set of elementary reactions in the most general form[1–4].

Autoxidation

$$2RH + O_2 \xrightarrow{k_0} 2\dot{R} + H_2O \ , \qquad (0)$$

$$RH + O_2 \xrightarrow{k_0'} \dot{R} + H\dot{O}_2 \ , \qquad (0')$$

$$\dot{R} + O_2 \xrightarrow{k_1} R\dot{O}_2 \ , \qquad (1)$$

$$\dot{R} \xrightarrow{k_{1'}} \dot{R}_1 + P_1 \ , \qquad (1')$$

$$R\dot{O}_2 + RH \xrightarrow{k_2} ROOH + \dot{R} \ , \qquad (2)$$

$$R\dot{O}_2 \xrightarrow{k_{2'}} R'COH + R''\dot{O} \ , \qquad (2')$$

$$R\dot{O}_2 + ROOH\ (ROH,\ R'COR'') \xrightarrow{k_{2''}} \dot{R}' + P_2 \ , \qquad (2'')$$

$$ROOH \rightarrow R\dot{O} + \dot{O}H \ , \qquad (3)$$

$$ROOH + RH\ (R_1COOH,\ R'COR'',\ \ldots) \xrightarrow{k_{3'}} 2\dot{R}'' + P_3 \ , \qquad (3')$$

$$ROOH + ROOH \xrightarrow{k_{3''}} R\dot{O} + R\dot{O}_2 + H_2O \ , \qquad (3'')$$

$$\dot{R}'\ (\dot{R}'',\ R\dot{O},\ \dot{O}H) + RH \rightarrow \dot{R}_4 + R'H\ (R''H,\ ROH,\ H_2O) \ , \qquad (4)$$

$$ROOH \rightarrow P_4 \ , \qquad (5)$$

$$R\dot{O}_2 + R\dot{O}_2 \rightarrow P_5 \ , \qquad (6)$$

$$R\dot{O}_2 \rightarrow \dot{\rho} \ . \qquad (6')$$

Inhibited oxidation

$$R\dot{O}_2 + InH \rightarrow In^{\cdot} + ROOH \ , \qquad (7)$$

$$\dot{R} + InH \rightarrow In^{\cdot} + RH \ , \qquad (7')$$

$$\dot{R} + Q \rightarrow P_6 \ , \qquad (7'')$$

$$ROOH + \rangle SH\ (\rangle PH) \rightarrow P_7 \ , \qquad (7''')$$

$$R\dot{O}_2 + In^{\cdot} \rightarrow InOOR \ . \qquad (8)$$

Catalysed oxidation

$$Cat + O_2 \rightleftharpoons Cat \ldots O_2 \xrightarrow{+RH} \dot{R} \ , \qquad (9)$$

$$Cat + RH \rightleftharpoons Cat \ldots RH \xrightarrow{+O_2} \dot{R} \ , \qquad (10)$$

$$Cat + R\dot{O}_2 \rightarrow Cat \ldots R\dot{O}_2 \begin{cases} \xrightarrow{+RH} P_8 + \dot{R} \ , & (11) \\ \rightarrow \text{chain termination.} & (12) \end{cases}$$

Here $\dot{p}$ is an inactive radical, InH a phenol or an amine, Q an inhibitor reacting with alkyl radicals, Cat a homogeneous or heterogeneous catalyst, $\rangle SH(\rangle PH)$ a sulphur-containing (or phosphorus-containing) inhibitor which reacts with hydroperoxides, and P_i are products.

For a long time, the detection and identification of the active centres of chain reactions (free radicals and atoms) were regarded as a kind of unique achievements. The wide-scale application of electron paramagnetic resonance (EPR) method altered the situation. The existence of free radicals has been detected by EPR in low-temperature oxidation reactions of various hydrocarbons. In many cases the spectra consist of a singlet with a g-factor of 2.015; the absorption line width depends on the structure of the peroxy-radicals and varies from 6 to 30 G (Fig.1, Table 1).[5-7]

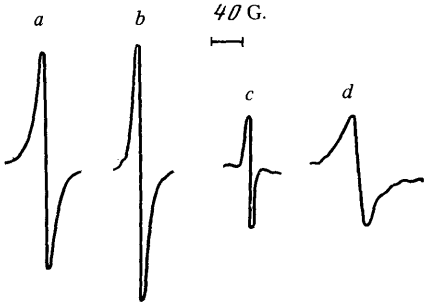


Figure 1. EPR spectra of peroxy-radicals in the oxidation of various substances: *a*) of cumene, catalysed by cobalt stearate, $[CoSt_2] = 1$ g litre^{-1}, 90 °C; *b*) of decalin, initiated by dicyclohexyl percarbonate, [PC] = 0.1 M, 85 °C; *c*) of 1,1′-diphenylethane, initiated by dicyclohexyl percarbonate, [PC] = 0.13 M, 69 °C; *d*) of iso-octane, initated by dicyclohexyl percarbonate, 78 °C.[5]

The formation of free radicals (chain initiation) in liquid-phase oxidation processes takes place as a rule in the bimolecular interaction of oxygen with the organic compound via reaction (0′).[3] A termolecular chain initiation reaction [reaction (0)] was discovered in the 1960's in relation to the oxidation of cyclohexanol and cyclohexanone[8-10]. The possibility of this reaction was subsequently confirmed in relation to the oxidation of n-decane[11], tetralin[9,12], and indan[12] (Table 1).

The termolecular mechanism of chain initiation can involve an intermediate stage in which a complex is formed in accordance with the scheme

$$RH + O_2 \rightleftarrows RH \ldots O_2 \ ,$$
$$RH \ldots O_2 + RH \rightarrow 2\dot{R} + H_2O_2 \ .$$

The formation of such complexes has been demonstrated spectrophotometrically[12].

In a fully developed oxidation process radicals are formed via degenerate chain branching. The rate of degenerate branching can be determined from the consumption of the inhibitor introduced into the reaction mixture at various stages of the oxidation process. It has been shown by this method, for example, in the study of Knorre et al.,[16] that in oxidation of n-decane the hydroperoxide is the only branching product. The chain branching rate constant $k_3 = 6 \times 10^8 \exp(-24\,800/RT)$ (s^{-1}).[16]

Table 1. The rate constants for chain initiation in the oxidation of various organic compounds.

Substance	A_0', litre mol^{-1} s^{-1}	E_0', kcal mol^{-1}	A_0, litre^2 mol^{-2} s^{-1}	E_0, kcal mol^{-1}	Refs.
	Bimolecular reaction (0′)		Termolecular reaction (0)		
Cyclohexane	$8.0 \cdot 10^{12}$	40.0			[15]
Isopropylbenzene	$3.5 \cdot 10^{9}$	27.4			[15]
o-Xylene	$2.0 \cdot 10^{8}$	31.0			[15]
Ethyl methyl ketone	$3.0 \cdot 10^{9}$	30.0			[13]
Ethanol	$6.0 \cdot 10^{7}$	30.0			[13]
Phenol	$7.0 \cdot 10^{12}$	35.0			[14]
p-Methoxyphenol	$7.5 \cdot 10^{9}$	27.0			[14]
p-Cresol	$3.0 \cdot 10^{11}$	32.0			[14]
α-Naphthol	$2.2 \cdot 10^{9}$	25.0			[14]
β-Naphthol	$4.5 \cdot 10^{10}$	29.0			[14]
α-Naphthylamine	$1.5 \cdot 10^{10}$	30.0			[14]
α-Naphthylphenylamine	$2.8 \cdot 10^{10}$	31.0			[14]
β-Naphthylphenylamine	$3.5 \cdot 10^{10}$	32.0			[14]
Tetralin			$4 \cdot 10^{3}$	20.7	[9]
Indan			$3.9 \cdot 10^{3}$	18.8	[12]
Cyclohexanol			8.3	16.0	[10]
Cyclohexanone			$2.1 \cdot 10^{2}$	17.5	[9]

Degenerate chain branching can occur not only as a result of the unimolecular decomposition of the hydroperoxide via reaction (3) but also via the bimolecular reaction (3′) with participation of the hydrocarbon. According to reaction (3′), the rate of branching decreases linearly with increasing hydrocarbon concentration[3].

With the decrease of the C–H bond strength in the hydrocarbon molecule in the sequence decane > 2,7-dimethyloctane > ethylbenzene > methyl oleate, the rate of decomposition of n-decyl hydroperoxide into radicals increases, which constitutes yet another piece of evidence for the occurrence of the bimolecular chain branching reaction (3′).[17]

At high hydroperoxide concentrations, which are particularly characteristic of the oxidation of α-olefins, the decomposition of the hydroperoxides and hence the degenerate chain branching take place via reaction (3″), the occurrence of which is promoted by the formation of hydrogen-bonded associated species:

$$ROOH + HOOR \rightleftharpoons [ROOH \ldots HOOR] \rightarrow R\dot{O} + R\dot{O}_2 + H_2O \ .$$

For high degrees of reaction, the products accumulating in the reaction mixture begin to participate in the chain branching. Organic acids, capable of forming a 2 : 1 complex with hydroperoxides, are important in this sense. Under the

influence of intermolecular hydrogen bonds, the dissociation of the O–O bond in the hydroperoxide molecule in such a complex is facilitated, which leads to the formation of free radicals[18,19]:

$$ROOH + 2RCOOH \overset{K}{\rightleftarrows} [ROOH \ldots 2RCOOH] \rightarrow R\dot{O} + \dot{O}H + 2RCOOH .$$

A study of the mechanism of chain propagation established that, as for gas-phase reactions, the liquid-phase oxidation reactions of organic compounds include in certain cases, together with the main chain propagation reaction

$$R\dot{O}_2 + RH \rightarrow ROOH + \dot{R} , \qquad (2)$$

also the isomerisation of peroxy-radicals accompanied by the decomposition of the radical with dissociation of the C–C bond and the formation of carbonyl compounds and radicals:

$$R\dot{O}_2 \rightarrow R'CHO + R''\dot{O} . \qquad (2')$$

The chain propagation in the oxidation of α-olefins constitutes two parallel reactions, in one of which the peroxy-radicals interact with the C–H bond [reaction (2)] with formation of hydroperoxides, while in the other peroxy-radicals add to the unsaturated bond [reaction (2‴)].[20] This reaction pathway leads to the formation of oxides, polyperoxides, and other products:

$$R\dot{O}_2 + \diagdown\!\!\diagup C\text{–}H\,(RH) \rightarrow ROOH + \dot{R} , \qquad (2)$$

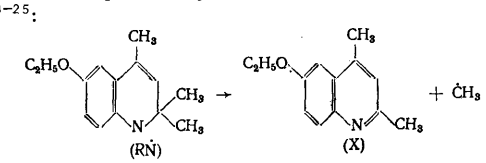
$$R\dot{O}_2 + \diagdown C{=}C\diagup\,(RH) \rightarrow R\dot{O}_2\text{–}\underset{|}{C}\text{–}\dot{C}\diagup \rightarrow \text{products.} \qquad (2''')$$

The rates of reactions (2) and (2‴) have been determined from the accumulation of hydroperoxides and the consumption of double bonds[21,22] in the oxidation of cyclohexene and phenylcyclohexene.

The rate constants k_2 and $k_{2'''}$ were calculated from the parameters $k_2/k_6^{1/2}$ and $k_{2'''}/k_6^{1/2}$ and the rate constant k_6 for the recombination of peroxy-radicals (determined by the method of interrupted illumination). The corresponding rate constants have the following values (in litre mol^{-1} s^{-1}): $k_2 = 5.7 \times 10^4 \exp[(-6300 \pm 300)/RT]$, $k_{2'''} = 1.4 \times 10^9 \exp[(-14\,000 \pm 600)/RT]$, and $k_6 = 1.5 \times 10^6$ for cyclohexene[21,22] and $k_2 = 2.2 \times 10^5 \exp[(-5000 \pm 300)/RT]$, $k_{2'''} = 1.4 \times 10^8 \exp[(-8400 \pm 300)/RT]$, and $k_6 = 2.5 \times 10^8$ for phenylcyclohexene[21,22].

The conjugation of the C=C bond with the phenyl group increases the reactivity of the α-olefin, which is manifested by a considerable decrease of the activation energy for the addition of the peroxy-radicals to the unsaturated bond in phenylcyclohexene relative to cyclohexene. It is also striking that there is a considerable increase of k_6 following the introduction of the phenyl substituent into the cyclohexene molecule, whereas by analogy with the corresponding alkanes, a lower value of k_6 for phenylcyclohexene relative to cyclohexene should have been expected in view of the steric effect of the substituent (the values of k_6 for cyclohexane and phenylcyclohexane are respectively 1.6×10^6 and 1.6×10^5 litre mol^{-1} s^{-1}).

In the oxidation of 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline (ethoxyquin) the rate-limiting stage in the chain propagation reaction is the decomposition of the primary free radical accompanied by the elimination of the methyl radical[23–25]:



(13)

The rate constant for this reaction is $k_{13} = 1.3 \times 10^{13} \exp(-20\,800/RT)$ (litre mol^{-1} s^{-1}).

At elevated temperatures this reaction leads to the formation of 6-ethoxy-2,6-dimethylquinoline (X) (Fig. 2) with a a selectivity up to 90% in chlorobenzene and more than 60% in n-decane, cumene, styrene, and phenylacetylene. At $t > 100$ °C the oxidation of ethoxyquin is a chain process.

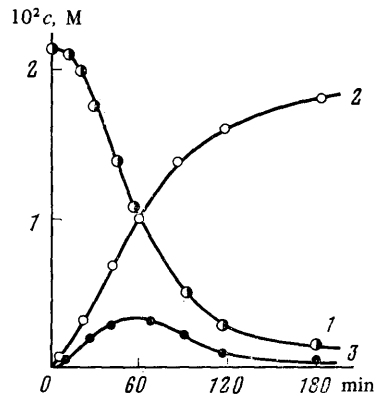
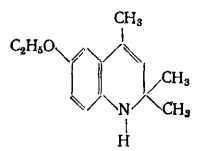


Figure 2. Kinetic curves for the consumption of ethoxyquin (curve *1*), the accumulation of the quinoline product (curve *2*), and the accumulation of methyl hydroperoxide (curve *3*) in the autoxidation of ethoxyquin in chlorobenzene (110 °C, oxygen flow rate 0.5 litre h^{-1}).[24]

The active centres for the chains are the free radicals RṄ, ĊH$_3$, and CH$_3$Ȯ$_2$ participating in the reactions

$$\dot{C}H_3 + O_2 \rightarrow CH_3\dot{O}_2 , \qquad (14)$$



$$+ CH_3\dot{O}_2\,(R\dot{O}_2,\ R\dot{O}) \rightarrow R\dot{N} + CH_3O_2H\,(RO_2H,\ ROH) , \qquad (15)$$

$$R\dot{N} + R\dot{N} \rightarrow RN\text{–}NR . \qquad (16)$$

The rate constant for the reaction of peroxy-radicals with the N–H bond of ethoxyquin is very high ($k_{15} \geq 10^6$ litre mol^{-1} s^{-1}) and does not limit the rate of oxidation. The rate constant for the recombination reaction (16), measured by flash photolysis, is $2k_6 = 9.8 \times 10^6$ litre mol^{-1} s^{-1} (20 °C, benzene).[26] Chain branching proceeds via a reaction of type (3′):

$$RNH + CH_3OOH\,(ROOH) \rightarrow R\dot{N} + CH_3\dot{O}(R\dot{O}) + H_2O .$$

In inert solvents this reaction proceeds with participation of methyl hydroperoxide.

At low temperatures, where the rate of decomposition of the radical RṄ via reaction (13) is low, ethoxyquin is one of the most effective antioxidants, since the rate constant for the interaction of peroxy-radicals with ethoxyquin [reaction (15)] is significantly greater than, for example, the corresponding constant for ionol ($k = 2 \times 10^4$ litre mol^{-1} s^{-1}, 60 °C [3]) and the RṄ radical formed is relatively inactive.

In hydrocarbons undergoing oxidation the RṄ radicals partly undergo a cross recombination reaction:

$$R\dot{N} + R\dot{O}_2 \rightarrow \text{products},$$

as a result of which the stoichiometric inhibition coefficient for ethoxyquin is greater than unity ($f \cong 1.3$ for the oxidation of phenylacetylene, styrene, ethylbenzene, and β-carotene; 50–60 °C).

Above 100 °C, the inhibiting efficiency of ethoxyquin falls in the oxidation of ethylbenzene, n-decane, and styrene, since the methylperoxy-radical formed in stage (15) is involved in the transfer of the hydrocarbon oxidation chain. The interaction of ethoxyquin with hydroperoxides plays a significant role in decreasing its efficiency as an inhibitor.

Ethoxyquin is an effective antioxidant for phenylacetylene even at a relatively high temperature. The inhibition is then due to the ethoxyquin reaction product—the corresponding quinoline.

The reactivity of the $R\dot{O}_2$ radicals with respect to the oxidation products [reaction (2″)] was determined by special kinetic procedures[27,28]; it was shown that, in the oxidation of n-decane, the ratios of the rate constant for reaction (2) (k_2) and the rate constants for the chain propagation as a result of the interaction of the radical $R\dot{O}_2$ with the alcohol ($k_{2''}$,ROH) and the hydroperoxide ($k_{2''}$,ROOH) are $k_2 : k_{2''},\mathrm{ROH} : k_{2''},\mathrm{ROOH} = 1 : 6 : 13$. The activation energies for the elementary stages[29,30] are $E_2 = 14.5$ kcal mol^{-1} and $E_{2''},\mathrm{ROH} = E_{2''},\mathrm{ROOH} = 10$ kcal mol^{-1}.

Thus the oxidation products are extremely reactive and have a significant influence on the oxidation mechanism.

The reactions of the $R\dot{O}_2$ radical with peroxides, alcohols, and ketones involve the interaction of two dipoles, which is significantly influenced by the dielectric constant of the medium.

The composition of the products of the oxidation of ethyl alcohol and ethyl methyl ketone at a pressure of 50 atm and a temperature of ~150 °C in a stainless steel reactor[32,33] is determined by the competition of two elementary chain propagation stages [reactions (2) and (2′)]. The principal oxidation products of ethyl methyl ketone are acetic acid, ethyl acetate, and diacetyl. In the oxidation of ethyl alcohol the products of the bimolecular reaction of the $R\dot{O}_2$ radical, namely acetic acid and ethyl acetate, constitute 80% of the total oxidation products. When ethyl methyl ketone and ethyl alcohol are diluted by a non-polar substance (benzene) the amount of the decomposition products of the $R\dot{O}_2$ radicals increases, because the addition of benzene diminishes the dielectric constant of the medium and the rate of reaction (2) falls.

The activation energy for reaction (2) in the oxidation of ethyl methyl ketone and ethyl alcohol increases with decrease of the dielectric constant of the medium[34]. The dipole moment of the activated complex $\mu_{\neq} = 8.4$ D, obtained from experimental data for the oxidation of ethyl methyl ketone, agrees well with the value calculated for one of the structures of the activated complex (8.1 D), i.e. in the case of ethyl methyl ketone the rate of reaction (2) is influenced solely by the dielectric constant of the medium. Not only the polarity of the medium but also the association of the alcohol via intermolecular hydrogen bonds plays an important role in the oxidation of the alcohol.

Chain termination in liquid-phase chain reactions takes place in the vast majority of cases via a quadratic recombination or disproportionation [reaction (6)] mechanism. The quadratic chain termination in the oxidation of hydrocarbons is apparently a complex process proceeding via a multistage mechanism[35–37]. According to Russell[38], the disproportionation of primary and secondary peroxy-radicals proceeds via an intermediate stage involving the formation of a cyclic complex, although it has been suggested that the process proceeds via a more complicated mechanism involving a zwitterion formation stage[37].

Tertiary peroxy-radicals probably interact via the mechanism

$$2R\dot{O}O \begin{cases} \rightarrow ROOR + O_2 , & (17a) \\ \rightarrow 2R\dot{O} + O_2 . & (17b) \end{cases}$$

The t-alkoxy radicals decompose with formation of a ketone and a low-molecular-weight primary radical, which is subsequently involved in disproportionation cross-reactions with the radicals $R\dot{O}O$.

For example, the radical $\dot{C}H_3$ is formed in the decomposition of the cumenyloxy-radical:

$$\begin{gathered} C_6H_5C(CH_3)_2\dot{O} \rightarrow C_6H_5(C{=}O)CH_3 + \dot{C}H_3 , \\ \dot{C}H_3 + O_2 \rightarrow CH_3\dot{O}_2 , \\ CH_3\dot{O}_2 + R\dot{O}_2 \rightarrow H_2CO + O_2 + ROH . \end{gathered} \qquad (18)$$

It is noteworthy that much attention has been devoted recently in the literature on the liquid-phase oxidation mechanism to the $R\dot{O}_2$ disproportionation reaction [reaction (17b)] as the chain propagation stage in the oxidation of hydrocarbons with tertiary[39] and secondary[40] C–H bonds.

A recent study[41] of the quadratic chain termination in the oxidation of cumene by the chemiluminescence method showed that the primary cumenylperoxy-radicals $C_6H_5CH(CH_3)CHO\dot{O}$, involved in the disproportionation cross-reactions

$$R\dot{O}O + C_6H_5CH(CH_3)CH_2O\dot{O} \rightarrow ROH + O_2 + C_6H_5CH(CH_3)CHO , \qquad (19)$$

play a major role in chain termination. Despite the low concentration of the primary peroxy-radicals, the contribution of reaction (19) to the overall rate of recombination is then comparable to the contribution of reaction (17) and greatly exceeds that of reaction (18) in the chain termination mechanism.

Various non-stationary methods are used to measure k_6, including rapid chemiluminescence (CL) methods[35,42]. A novel chemiluminescence method has been recently developed for the determination of the recombination and disproportionation constants of free peroxy-radicals in cases where the relevant processes are not accompanied by intense luminescence sufficient for its measurement under non-stationary conditions[43]. The method is based on the measurement of the non-stationary chemiluminescence in the coupled oxidation of the test substance RH with a small amount of an added "standard" compound R_1H characterised by fairly high chemiluminescence yields in chain termination processes. Non-stationary conditions are obtained as a result of the rapid introduction of an initiator into the system. The chemiluminescence arising in the coupled system is due to the reactions

$$\begin{gathered} R\dot{O}_2 + R_1\dot{O}_2 \rightarrow \text{products}, \\ R_1\dot{O}_2 + R_1\dot{O}_2 \rightarrow \text{products}. \end{gathered}$$

The ratio of the concentrations of the radicals $R\dot{O}_2$ and $R_1\dot{O}_2$ is determined by the rates of the chain propagation cross-reactions

$$R\dot{O}_2 + R_1H \rightarrow ROOH + \dot{R}_1 , \qquad (22)$$

$$R_1\dot{O}_2 + RH \rightarrow R_1OOH + \dot{R} . \qquad (23)$$

The effective rate constant for the recombination of radicals k_6^{eff} in mixtures of different composition is described by the formula

$$\ln \frac{1 + (I/I_\infty)^{1/2}}{1 - (I/I_\infty)^{1/2}} = 2(w_i k_6^{\mathrm{eff}})^{1/2} t$$

(I is the chemiluminescence intensity and I_∞ the limiting value of I for the given rate of chain initiation w_i), analogous to that used to decribe the non-stationary kinetics in the oxidation of pure hydrocarbons[42]. The constant k_6^{eff} varies

linearly with mixture composition and is given by an expression of the form

$$k_6^{\text{eff}} = k_6 + 2\frac{k_{22}}{k_{23}}(k_{20} - k_{21})\frac{[R_1H]}{[RH]},$$

which makes it possible to calculate the required constant k_6 from the dependence of k_6^{eff} on the ratio $[R_1H]/[RH]$. The method has been used[44] to determine k_6 for the oxidation of substituted 3-phenylindans.

In certain special cases there is apparently a possibility also of linear termination together with quadratic chain termination in liquid-phase oxidation reactions. A change of the chain termination reaction[45-47] from quadratic to linear with increase of temperature has been established in a study of the kinetics of the oxidation of unsaturated compounds: 4-(2,6,6-trimethyl-1-cyclohexenyl)but-3-en-1-one (β-ionone) and the acetoacetate ester of the corresponding alcohol (β-ionol acetate). At temperatures below 70 °C the rate of oxidation of these compounds w varies in proportion to $w_i^{1/2}$, which is a kinetic feature of quadratic chain termination; at 70–80 °C the variation of w is proportional to w_i, which indicates the predominance of linear termination in this case (Fig. 3). Kinetic analysis has shown that the linear chain termination is due to the isomerisation of the free peroxy- or alkyl-radicals involved in the chain propagation[45]:

$$RO_2^{\cdot}(R^{\cdot}) \rightarrow \dot{\rho}\,. \qquad (6')$$

The change in the chain termination mechanism is accompanied by a relative decrease of the rate of reaction.

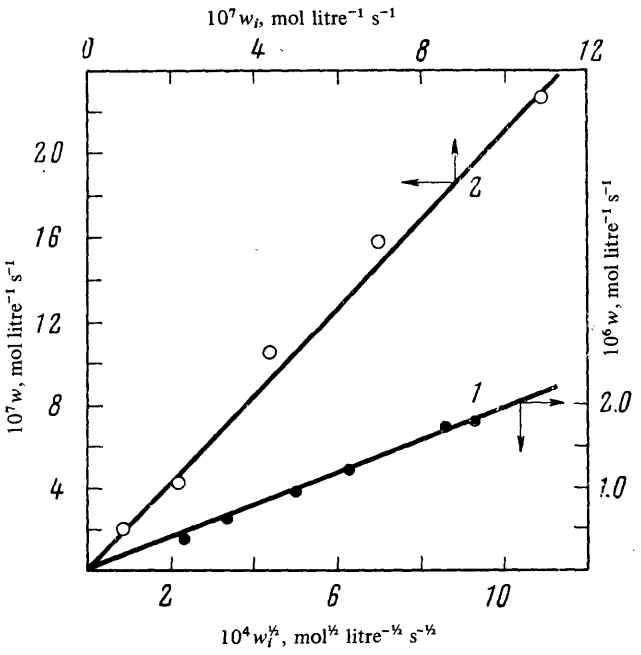


Figure 3. Dependence of the rate of absorption of oxygen in the initiated oxidation of β-ionone at 60 °C on $w_i^{1/2}$ (line 1) and at 85 °C on w_i (line 2); β-ionone concentration (M): 1) 0.09; 2) 0.1; initiators: 1) azobisisobutyronitrile; 2) benzoyl peroxide; solvent—chlorobenzene[46].

2. Oxidation Kinetics

In order to analyse the characteristics of the degenerate branched chain oxidation reactions of organic compounds occurring over a period of time, it is possible to examine a simplified mechanism reflecting the principal kinetic types of the elementary reactions of the initial compound (RH), the active centres—peroxy-radicals ($RO_2^{\cdot}$), and the intermediates (ROOH) involved in the formation of free radicals. In conformity with the detailed mechanism presented above, the following reactions are involved†:

$$\left.\begin{array}{l} RH + RO_2^{\cdot} \xrightarrow{k_2} RO_2^{\cdot} + ROOH, \\ \qquad\qquad \xrightarrow{k_2'''} RO_2^{\cdot} + \text{products}; \end{array}\right\} \text{(chain propagation)}$$

$$\left.\begin{array}{l} RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_6} P_6, \\ RO_2^{\cdot} \xrightarrow{k_{6'}} \rho\,; \end{array}\right\} \text{(chain termination)}$$

$$\left.\begin{array}{l} RH \xrightarrow{k_0} RO_2^{\cdot}, \\ ROOH \xrightarrow{k_3} RO_2^{\cdot}, \\ ROOH + ROOH \xrightarrow{k_{3''}} RO_2^{\cdot}. \end{array}\right\} \text{(chain initiation)}$$

The kinetic equations for the rate of a reaction proceeding via the above mechanism at quasi-stationary concentrations of free radicals are

$$w_i - k_6[RO_2^{\cdot}]^2 - k_{6'}[RO_2^{\cdot}] = 0\,, \qquad (24)$$

$$-\mathrm{d}[RH]/\mathrm{d}t = k_2[RO_2^{\cdot}][RH]\,, \qquad (25)$$

$$-\mathrm{d}[ROOH]/\mathrm{d}t = \alpha k_2[RO_2^{\cdot}][RH] - k_3[ROOH] - k_{3''}[ROOH]^2\,, \qquad (26)$$

$$w_i = k_0[RH] + \delta k_3[ROOH] + \delta k_{3''}[ROOH]\,, \qquad (27)$$

where δ is the number of free radicals per ROOH molecule decomposed and α is a parameter defining the fraction of ROOH in the sum of products formed in the chain propagation stages.

It follows from Eqns. (24) and (25) that in quadratic chain termination, where $k_6[RO_2^{\cdot}] \gg k_{6'}$, we have

$$[RO_2^{\cdot}] = (w_i/k_6)^{1/2},$$
$$-\mathrm{d}[RH]/\mathrm{d}t = k_2[RH](w_i/k_6)^{1/2}, \qquad (28)$$

while in linear termination, where $k_{6'} \gg k_6[RO_2^{\cdot}]$, we have

$$[RO_6^{\cdot}] = w_i/k_{6'},$$
$$-\mathrm{d}[RH]/\mathrm{d}t = k_2[RH](w_i/k_{6'}). \qquad (29)$$

The study of the kinetics of the oxidation of organic compounds of different classes led to the derivation of various functions $w_i = w_i\{[RH]\}$ and the corresponding overall kinetic equations. Up to a certain degree of conversion, particularly in the initial stages, the amount of compound consumed may be proportional to the ROOH concentration:

$$[ROOH] = \alpha([RH]_0 - [RH]). \qquad (30)$$

† The following assumptions have been made: all the radicals, including alkyl, alkoxy-, and hydroxy-radicals, are rapidly converted into peroxy-radicals: $\dot{R} + O_2 \rightarrow RO_2^{\cdot}$; $RO(OH)^{\cdot} + RH \rightarrow \dot{R}$ + products; the chain length is small, which makes it possible to neglect the consumption of RH associated with the formation of free radicals other than peroxy-radicals in the stage involving the decomposition of the intermediates (chain initiation). The product (ROOH) involved in chain branching is formed in one of the chain propagation reactions.

In this case Eqn.(27) can be put in the form

$$w_i = k_0[RH] + \alpha\delta k_3([RH]_0 - [RH]) + \alpha^2\delta k_{3''}([RH]_0 - [RH])^2 . \quad (31)$$

Eqn.(31) holds when the consumption of ROOH can be neglected in Eqn.(26) or when there are several compounds formed consecutively and decomposing into free radicals.

Integration of Eqn.(28) or (29) leads to different expressions, depending on the ratios of the rate constants for the chain initiation stages. We shall examine several cases.

1. The decomposition of ROOH is a first-order reaction and the chain termination is quadratic: $k_3 \gg k_{3''}[ROOH]$; $k_{6'} = 0$. In this case Eqn.(31) and the solution of Eqn.(28) are

$$w_i = k_0[RH] + \alpha\delta k_3([RH]_0 - [RH]) \quad (32)$$

$$\ln\frac{1 + (1 - [RH]/[RH]_0)^{1/2}}{1 - (1 - [RH]/[RH]_0)^{1/2}} = c_1 t, \quad (33)$$

where $c_1 = k_2\{\alpha\delta k_3[RH]_0/k_6\}^{1/2}$ is a parameter.

Eqn.(33) holds in the oxidation of β-carotene and phenylcyclohexene (at temperatures below 90 °C).[48,49] Eqn.(32) has been derived experimentally by determining w_i during the reaction by the method of inhibitors. In most cases Eqn.(32) holds in the initial stages of the reaction where its extent is low and one can assume that $[RH] \cong [RH]_0$; formula (33) can then be fitted by the equation of a parabola:

$$[ROOH] = c_1'' t^2 \quad (34)$$

where $c_1'' = 0.25\alpha^2 k_2^2[RH]_0^2\delta k_3/k_6$ is a parameter. Hydroperoxides accumulate in accordance with a parabolic law in the oxidation of aromatic alkyl-substituted hydrocarbons and paraffinic hydrocarbons in the initial stages of the reaction[50].

2. The decomposition of ROOH is a second-order reaction and the chain termination is quadratic: $k_{3''}[ROOH] \gg k_3$; $k_0 \ll k_{3''}[ROOH]$; $k_{6'} = 0$.

Function (31) and the solution of Eqn.(28) then become

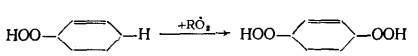
$$w_i = \alpha^2\delta k_{3''}([RH]_0 - [RH])^2$$
$$\ln\frac{([RH]_0 - [RH])}{[RH]} = \frac{\alpha k_2(\delta k_{3''})^{1/2}[RH]_0}{k_6^{1/2}}t + \text{const} . \quad (35)$$

Using Eqn.(30), it is possible to obtain from Eqn.(35) an expression for the accumulation of the hydroperoxide:

$$\ln\frac{[ROOH]}{\alpha[RH]_0 - [ROOH]} = \frac{\alpha k_2(\delta k_{3''})^{1/2}[RH]_0}{k_6^{1/2}}t + \text{const} . \quad (36)$$

Eqns.(35) and (36) have been obtained for the consumption of cyclohexene and the accumulation of cyclohexenyl hydroperoxide in the autoxidation of cyclohexene[49] up to a degree of conversion of ~20% (Fig.4).

The main pathway in the consumption of cyclohexenyl hydroperoxide involves its oxidation via a chain mechanism with participation of the C–H bonds, as in the initial cyclohexene:



(37)

This process determines the maximum concentration of the intermediate and the rate of formation of free radicals. The main product of the reaction of a monohydroperoxide is the dihydroperoxide (Fig.4, curve 3).

Cyclohexenyl hydroperoxide is more reactive in reactions with peroxy-radicals than is cyclohexene. Thus, for a degree of reaction in excess of 20% (at 70 °C), the cyclohexene undergoing oxidation is a multicomponent system in which the initial compound is consumed under the conditions of its joint oxidation with the primary reaction product.

3. The product ROOH and the initial compound have similar reactivities in the formation of free radicals and the chain termination is linear: $\delta k_3 \cong k_0$; $k_6 = 0$.

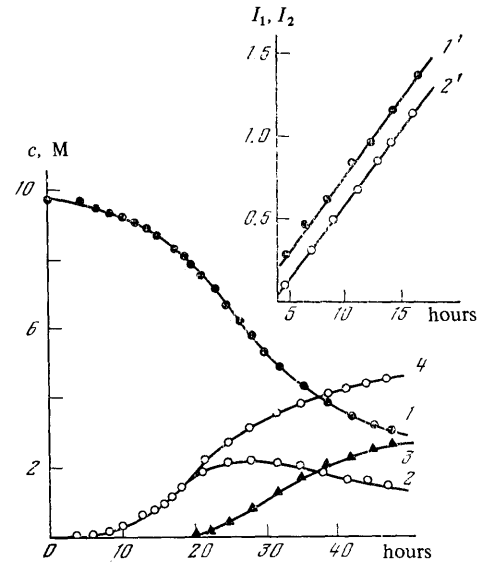


Figure 4. *a*) Kinetic curves for the consumption of cyclohexene (curve *1*), the accumulation of cyclohexenyl hydroperoxide (curve *2*), the accumulation of dihydroperoxide (curve *3*), and the sum of peroxides (curve *4*) in the oxidation of cyclohexene in a closed vessel under the conditions of the saturation of the liquid phase with oxygen; *b*) transformed kinetic curves for the consumption of cyclohexene (curve *1'*) and the accumulation of cyclohexenyl hydroperoxide (curve *2'*) in terms of the variables of Eqns.(35) and (36) up to a 20% degree of conversion of the hydrocarbon; 70 °C; $I_1 = 2 + \lg(\{[RH]_0 - [RH]\}/[RH])$; $I_2 = 2 + \lg([ROOH]/\{\alpha[RH]_0 - [ROOH]\})$ for $\alpha = 0.7$.[49]

In this case the decrease of w_0 as a consequence of the consumption of the compound is compensated by the increase of w_p and as a result the overall rate of formation of free radicals hardly changes in the course of the process. Eqn.(29) and the solution of Eqn.(28) have the form

$$w_i = k_3[RH]_0 , \quad (38)$$

$$[RH] = [RH]_0\exp(-c_3 t) . \quad (39)$$

where $c_3 = k_2\delta k_3[RH]_0/k_{6'}$ is an effective first-order rate constant.

Eqn.(38) and the first-order kinetic equation (39) have been obtained[45] for the oxidation of the unsaturated compound 4-(2,6,6-trimethyl-1-cyclohexenyl)but-3-en-2-yl acetate (β-ionol acetate) (Fig.5). In this case the first-order equation merely simulates a complex chain mechanism. This is indicated, for example, by the dependence of the effective rate constant c_3 on the initial concentration of the compound (Fig.5).

Phenylacetylene is apparently oxidised in accordance with a first-order equation with linear chain termination. This process constitutes oxidative polymerisation with a very small contribution by stages of the oxidative-degrative type[51].

In the oxidation of ethyl methyl ketone the rate of formation of free radicals w_i remains constant up to the complete decomposition of the compound with quadratic chain termination[52]:

$$w_i = c = \text{const}. \quad (40)$$

This feature of the chain initiation is associated with the thermal decomposition in the course of the reaction of two consecutively formed intermediates—a ketohydroperoxide and diacetyl.

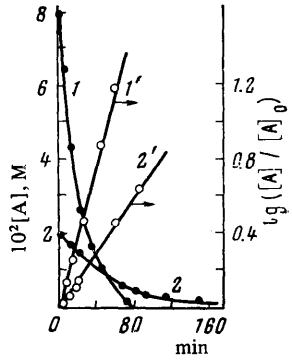


Figure 5. Kinetic curves for the consumption of β-ionol acetate (A) (curves *1* and *2*) and the semilogarithmic forms of the curves (curves *1'* and *2'*); solvent—chlorobenzene; 80 °C.[45]

Integration of Eqn.(28) leads to the expression

$$[RH] = [RH]_0 \exp(-c_3' t) \quad (41)$$

where $c_3' = k_2(w_i/k_6)^{1/2}$ is the effective rate constant. Thus we have a first-order equation, like Eqn.(39), but with another structure of the effective constant c_3'.

4. Free radicals are formed only with participation of the initial compound and the chain termination is quadratic: $k_0 \gg k_3$, $k_0 \gg k_{3''}[ROOH]$, $k_{6'} = 0$. According to Eqn.(31), the rate of chain initiation decreases in the course of the process:

$$w_0 = k_0[RH]\ . \quad (42)$$

Integration of Eqn.(28) leads to the expression

$$\frac{1}{[RH]_0^{1/2}} - \frac{1}{[RH]^{1/2}} = c_4 t\ , \quad (43)$$

where $c_4 = 0.5k^2(k_0/k_6)^{1/2}$ is a parameter.

Evidently Eqn.(43) is the kinetic equation of an unbranched chain reaction. Eqns.(42) and (43) have been obtained for the autoxidation of phenylcyclohexene above 90 °C.[49] For this cyclo-olefin, a change in the oxidation process conditions from degenerate branched (at t < 90 °C) to unbranched (at *t* > 90 °C) is observed due to the characteristics of the reactions of the intermediates.

The autocatalytic nature of the process at low temperatures is due to the formation in reaction (2) of unsaturated hydroperoxides, which readily decompose into free radicals. The main cause of the change in process conditions with increase of temperature is the oxidation of unsaturated hydroperoxides with participation of C=C bonds, leading to the formation of thermally stable compounds. At the same time the rate of reaction of phenylcyclohexene with oxygen (chain initiation) and the activity of the free radicals in chain propagation are sufficiently high for the reaction to develop at a high rate and without chain branching.

Thus the type of kinetic equation for the reaction is determined by the nature of the decomposition of the intermediates and the ratio of the reactivities of the initial compound and the intermediates in the formation of free radicals.

The overall kinetic equations contain the parameters c_1, c_2, etc., which can be determined from transformed kinetic curves. For autocatalytic reactions, the parameters of the equations contain the rate constants for chain propagation, termination, and degenerate branching: $c = k_2(\alpha\delta k_3/k_6)^{1/2}$. These parameters can serve as characteristics of the reactivity of organic compounds in oxidation processes.

3. Oxidation of Multicomponent Mixtures. Coupled Oxidation

In the coupled oxidation of binary mixtures of hydrocarbons R_1H and R_2H, two types of radicals, $R_1\dot{O}_2$ and $R_2\dot{O}_2$, which can interact with both hydrocarbons, are involved in chain propagation and termination[3]. As a result, together with the chain propagation and termination reactions occurring in the oxidation of the pure hydrocarbons R_1H and R_2H,[53–56] i.e.

$$\dot{R}_1 + O_2 \rightarrow R_1\dot{O}_2\ , \quad (1)$$

$$R_1\dot{O}_2 + R_1H \rightarrow R_1OOH + \dot{R}_1\ , \quad (2)$$

$$R_1\dot{O}_2 + R_1\dot{O}_2 \rightarrow \text{products}, \quad (6)$$

$$\dot{R}_2 + O_2 \rightarrow R_2\dot{O}_2\ , \quad (44)$$

$$R_2\dot{O}_2 + R_2H \rightarrow R_2OOH + \dot{R}_2\ , \quad (45)$$

$$R_2\dot{O}_2 + R_2\dot{O}_2 \rightarrow \text{products}, \quad (46)$$

chain propagation and termination cross-reactions also take place:

$$R_1\dot{O}_2 + R_2H \rightarrow R_1OOH + \dot{R}_2\ , \quad (47)$$

$$R_2\dot{O}_2 + R_1H \rightarrow R_2OOH + \dot{R}_1\ , \quad (48)$$

$$R_1\dot{O}_2 + R_2\dot{O}_2 \rightarrow \text{products}. \quad (49)$$

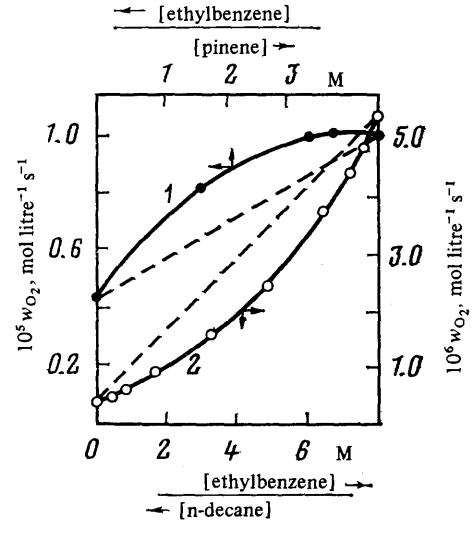


Figure 6. Dependence of the rate of oxidation on the composition of the mixtures of hydrocarbons: 1) pinene–ethylbenzene (70 °C); 2) n-decane–ethylbenzene (77 °C).

The occurrence of reactions (47)–(49) leads to the non-additive dependence of the rate of oxidation on the mixture composition (Fig.6).

Under the conditions of initiated oxidation, when the above joint oxidation mechanism is valid, the rate of absorption of oxygen is described by the formula

$$w_{O_2} = w_i^{1/2} \frac{r_1[R_1H]^2 + 2[R_1H][R_2H] + r_2[R_2H]^2}{((r_1^2/b_1^2)[R_1H]^2 + 2\Phi(r_1r_2/b_1b_2)[R_1H][R_2H] + (r_2^2/b_2^2)[R_2H]^2)^{1/2}}, \quad (50)$$

where $b_1 = k_2/k_6^{1/2}$, $b_2 = k_{45}/k_{46}^{1/2}$, $r_1 = k_2/k_{47}$, $r_2 = k_{45}/k_{48}$, and $\Phi = k_{49}/(k_6k_{46})^{1/2}$. This equation is used widely in the determination of the reactivity of peroxy-radicals with respect to a series of hydrocarbons (Table 2). Together with the chain propagation and termination "cross-reactions", reactions involving alkyl radicals can play a significant role in the oxidation of multicomponent mixtures[59–62]:

$$\dot{R}_1 + R_2H \rightarrow R_1H + \dot{R}_2, \quad (51)$$

$$\dot{R}_2 + R_1H \rightarrow R_2H + \dot{R}_1. \quad (52)$$

Table 2. The rate constants for the reactions $R_1\dot{O}_2 + R_2H \rightarrow R_1OOH + \dot{R}_2$ (75 °C).

R_2H	$R_1\dot{O}_2$	k_{47}, litre mol^{-1} s^{-1}	References
o-Xylene	allylbenzene	4.0	57
o-Xylene	tetralin	2.0	57
o-Xylene	α-methylstyrene	0.9	57
Cumene	allylbenzene	6.5	57
Cumene	tetralin	2.6	57
Cumene	α-methylstyrene	1.0	57
Ethylbenzene	allylbenzene	6.2	57
Ethylbenzene	tetralin	3.9	57
Ethylbenzene	α-methylstyrene	1.4	57
Ethylbenzene	2,7-dimethyloctane*	0.12	58
Allylbenzene	tetralin	19	57
Allylbenzene	α-methylstyrene	9.2	57
Tetralin	allylbenzene	44	57
Tetralin	α-methylstyrene	12	57
α-Methylstyrene	allylbenzene	400	57
α-Methylstyrene	tetralin	100	57
2,7-Dimethyloctane	ethylbenzene*	4.8	58
1-Methyl-3-phenylindan	ethylbenzene**	39.2	44
1,3-Dimethyl-3-phenylindan	ethylbenzene**	17.8	44
1,1-Dimethyl-3-phenylindan	ethylbenzene**	30.4	44

*At 77 °C.
**At 60 °C.

If account is taken of the possibility of competition between reactions (1) and (51) and between (44) and (52) in initiated oxidation, then Eqn.(50) is transformed into[63]

$$w_{O_2} = w_i^{1/2} \frac{k_2[R_1H] + k_{47}[R_2H] + c(k_{48}[R_1H] + k_{45}[R_2H])}{(2k_6 + 2k_{49}c + 2k_{46}c^2)^{1/2}}, \quad (53)$$

where

$$c = \frac{(k_{51}[R_2H]/k_1[O_2])(k_2[R_1H] + k_{47}[R_2H]) + k_{47}[R_2H]}{(k_{52}[R_1H]/k_{44}[O_2])(k_{48}[R_1H] + k_{45}[R_2H]) + k_{48}[R_1H]}.$$

Analysis of Eqn.(53) shows that reaction (51) influences most strongly the kinetics of the oxidation of nearly equimolar mixtures. The overall rate of oxidation is sensitive to reaction (51) with $k_{51} \geq 10^3$ litre mol^{-1} s^{-1}.

As a result of the large difference between the activation energies for the reactions of free radicals $\dot{R}_1$ with O_2 and R_2H, reaction (51) occurs to a large extent at high temperatures.

Degenerate chain branching reactions also play an important role in the non-initiated oxidation of multicomponent systems at 100–140 °C. The rate of degenerate branching is then determined by the rates of unimolecular and bimolecular decomposition of the hydroperoxides R_1OOH and R_2OOH:

$$\left.\begin{aligned} R_1OOH &\rightarrow \dot{R}_1\dot{O} + \dot{O}H, \\ R_2OOH &\rightarrow R_2\dot{O} + \dot{O}H, \end{aligned}\right\} \quad (3)$$

$$\left.\begin{aligned} R_1OOH + R_1H &\rightarrow R_1\dot{O} + \dot{R}_1 + H_2O, \\ R_2OOH + R_2H &\rightarrow R_2\dot{O} + \dot{R}_2 + H_2O, \\ R_1OOH + R_2H &\rightarrow R_1\dot{O} + \dot{R}_2 + H_2O, \\ R_2OOH + R_1H &\rightarrow R_2\dot{O} + \dot{R}_1 + H_2O. \end{aligned}\right\} \quad (3')$$

The occurrence of the new chain transfer reaction (51) as well as the branching reactions results in a sharp difference between the characteristics of the oxidation of multicomponent mixtures under these conditions and those of initiated oxidation. Thus, in the degenerate branched chain oxidation reaction of mixtures of ethylbenzene with paraffins (n-decane, 2,7-dimethyloctane, 130 °C), one observes an acceleration of the oxidation of n-decane by small amounts of added ethylbenzene instead of its retardation (as in initiated oxidation) (Fig.7). On further increase of the content of ethylbenzene in the mixture to 7.5 vol.%, the consumption of n-decane begins to be inhibited strongly and virtually ceases in the presence of ~10 vol.% of ethylbenzene in the mixture[60]. Under these conditions, virtually only ethylbenzene is oxidised. The maximum rate of oxidation of ethylbenzene is observed in the range of ratios of mixture components in which the maximum rate of oxidation of n-decane is attained.

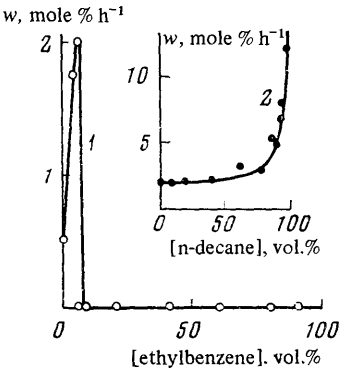


Figure 7. Dependence of the initial rate of oxidation of n-decane (curve *1*) and ethylbenzene (curve *2*) on the composition of the n-decane–ethylbenzene mixture; 130 °C.[60]

Mathematical analysis of the kinetic scheme of the coupled oxidation of two hydrocarbons (in relation to the oxidation of a mixture of n-decane and ethylbenzene at 130 °C), taking into account the chain transfer reaction (51) and the degenerate branching reactions (3)–(3'), showed[62] that the experimental dependence of the rates of oxidation of the mixture components on the mixture composition cannot be explained without taking into account reaction (51).

Thus, under the conditions of the high-temperature coupled oxidation of hydrocarbons, the set of elementary reactions making up the process mechanism greatly increases.

Reaction (51) must be taken into account particularly in the thermo-oxidative degradation of polymers, where the diffusion of O_2 into the polymer is difficult.

On the basis of coupled oxidation reactions, it is possible to devise technological processes in which the oxidising agents are highly reactive peroxy-radicals and not molecular oxygen. One of the substances being oxidised is then the source of peroxy-radicals, which interact with the second mixture component.

An example of such a reaction is the formation of epoxypropane and an organic acid by the joint (coupled) oxidation of aldehydes and olefins[64,65]. This process proceeds via the mechanism of a chain reaction and the main epoxidising agent is the acylperoxy-radical[66]:

$$RCOO\dot{O} + CH_2{=}CHCH_3 \rightarrow [RCOOO \cdot C_3H_6] \rightarrow -\overset{|}{C}-\overset{|}{C}- + R\dot{C}OO \ ,$$
$$\diagdown O \diagup$$

$$R\dot{C}OO + RH \rightarrow RCOOH + \dot{R} \ .$$

Together with the radical reaction, there is also a molecular pathway in the epoxidation of propene with peracetic acid (the Prilezhaev reaction[67]). However, the contribution of this reaction in the coupled acetaldehyde–propene process does not exceed 15 mole % of the overall rate of formation of epoxypropane. The concentration of dissolved oxygen has a significant influence on the rate of formation of epoxypropane[58].

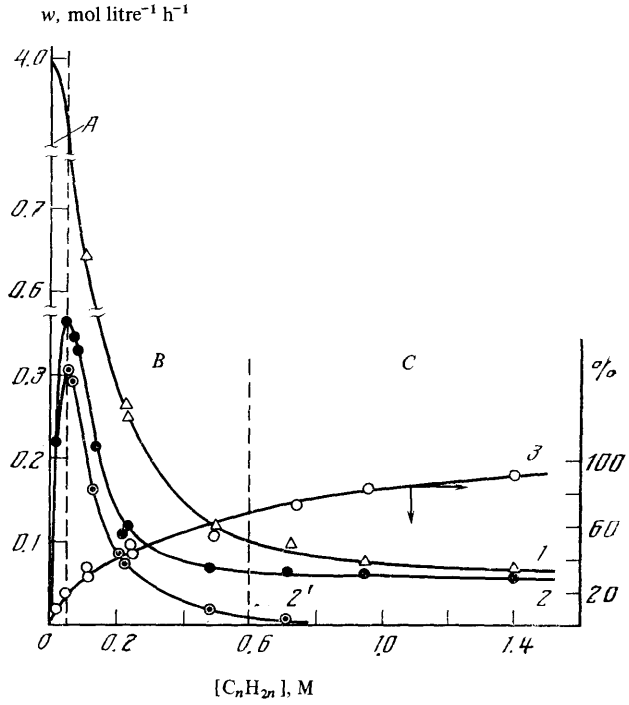


Figure 8. Dependence of the rate of consumption of benzaldehyde (curve *1*) and accumulation of epoxynonane (curve *2*) on the concentration of non-1-ene in chlorobenzene; *2'*) calculated curve for the rate of epoxidation of non-1-ene with perbenzoic acid; 3) variation of the yield of epoxynonane relative to the benzaldehyde which has reacted. Temperature 90 °C; rate of supply of oxygen 3 litres h^{-1}.[69]

The coupled oxidation of non-1-ene and benzaldehyde[69] is characterised by a nearly 100% selectivity in the formation of 1,2-epoxynonane relative to both initial reactants which have reacted—the olefin and the aldehyde. There is an extremum in the rate of formation of 1,2-epoxynonane as a function of the initial concentration of non-1-ene (Fig.8). The ratio of the rates in the two pathways leading to the formation of 1,2-epoxynonane (epoxidation by acylperoxy-radicals and the peracid) is determined by the composition of the initial mixture and the kinetic parameters of the system. At relatively low concentrations of the aldehyde the formation of epoxynonane has a radical mechanism, while at high values of [RCHO] the main epoxidising agent is the peracid.

In the coupled oxidation of olefins (C_nH_{2n}) and aldehydes (RCHO) an important role is played by the addition of acylperoxy-radicals to the double bond [reaction (60)], which is the main chain termination pathway, because the relatively inactive polyperoxy-radical $M\dot{O}_2$ formed under these conditions cannot enter into the exchange reaction (54) during the period of the propagation of the primary chain, i.e. the condition $1/k_{59}[C_nH_{2n}] < 1/k_{54}[RCHO]$ holds. The overall process mechanism can be formulated thus:

$$M\dot{O}_2 + RCHO \rightarrow RCOO\dot{O} + MOOH \ , \quad (54)$$

$$RCHO + O_2 \rightarrow R\dot{C}O + H\dot{O}_2 \ , \quad (55)$$

$$R\dot{C}O + O_2 \rightarrow RCOO\dot{O} \ , \quad (56)$$

$$RCOO\dot{O} + RCHO \rightarrow RCOOOH + R\dot{C}O \ , \quad (57)$$

$$RCOO\dot{O} + RCHO \rightarrow RCOOH + R\dot{C}O \ , \quad (58)$$

$$RCOO\dot{O} + C_nH_{2n} \rightarrow RCOO\dot{O} + \text{epoxide} \ , \quad (59)$$

$$RCOO\dot{O} + C_nH_{2n} \rightarrow M\dot{O}_2 \xrightarrow{k'_{60}} \dot{M} \xrightarrow{k''_{60}} M\dot{O}_2 \rightarrow \text{molecular products}, \quad (60)$$

$$RCOOOH + RCHO \rightarrow 2RCOOH \ , \quad (61)$$

$$RCOOOH + C_nH_{2n} \overset{K_{63}}{\rightleftarrows} RCOOOH \ldots C_nH_{2n} \rightarrow \text{epoxide} + RCOOH \ , \quad (62)$$

$$RCOOOH \ldots C_nH_{2n} \rightarrow RCOOH + {}^1/_2O_2 + C_nH_{2n} \ , \quad (63)$$

$$RCOO\dot{O} + RCOO\dot{O} \rightarrow \text{molecular products.} \quad (64)$$

When the proposed mechanism holds, the rate of formation of the epoxide (w_e) is described by the formula

$$w_e = \frac{k_{59}[C_nH_{2n}]w_i}{k + k_{60}[C_nH_{2n}]} + \frac{k_{57}k_{62}[RCHO]^2 w_i (1 + K_{63}[C_nH_{2n}])}{(k + k_{60}[C_nH_{2n}])\{k_{61}[RCHO] + (k_{62} + k_{63})K_{63}[C_nH_{2n}]\}} \quad (65)$$

where $k = k_{64}[RCOO\dot{O}]$. The first term in Eqn.(65) characterises the epoxidation of the olefin by the RCOOȮ radicals and the second characterises its epoxidation by the peracid (the Prilezhaev reaction).

The extremum in the relation between the rate of epoxidation and the olefin concentration is due to the molecular stage in the epoxidation of the olefin by the peracid, because in zone *B* (Fig.8) there is a sharp decrease of the steady-state concentration of the peracid in proportion to the square of the concentration of the olefin. The constancy of w_e as $[C_nH_{2n}]$ increases (zone *C*, Fig.8) is due to the radical component of the rate of oxidation; the role of the peracid becomes negligible. A 100% yield of 1,2-epoxynonane relative to the unconsumed benzaldehyde is characteristic of zone *C*. At low olefin concentrations (zones *A* and *B*, Fig.8) the incomplete utilisation of the active oxygen in epoxidation (Fig.8 curve *3*) is associated with reaction (61) and also with the molecular decomposition of the peracid induced by the olefin.

The rate constant for the epoxidation of the olefin by acylperoxy-radicals has been obtained for the joint oxidation of benzaldehyde and non-1-ene: $k_{54} = 1.8 \times 10^4$ litre mol^{-1} s^{-1}.

The mechanism of the coupled oxidation of olefins and aldehydes shows that the interaction of the RCOOȮ radical with an olefin leads to the formation of two new radicals—the active radicals RCȮ and the radicals $M\dot{O}_2$ which determine the

development of the polymerisation pathway in the system resulting in a decrease of the yield of the epoxide.

Analysis of the system showed that when the radicals $MO_2^{\cdot}$ are relatively inactive compared with RCO and do not participate in chain transfer to the aldehyde, the relative contributions of reactions (59) and (60) can be altered by a special procedure, which has come to be called selective inhibition[70] and thus the selectivity of the oxidation can be significantly increased by suppressing the undesirable reaction pathway as a result of the introduction of the appropriate inhibitor.

The selective inhibition method has been used to increase the yield of styrene oxide in the coupled oxidation of styrene and acetaldehyde[71] and to increase the yield of epichlorohydrin in the coupled oxidation of allyl chloride and acetaldehyde[72]. The inhibitor used was tanol (the 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy-radical). In the presence of this inhibitor, which interacts with the radicals $\dot{M}$, the polymerisation reaction pathway [reaction (60)] is almost completely arrested (Fig. 9).

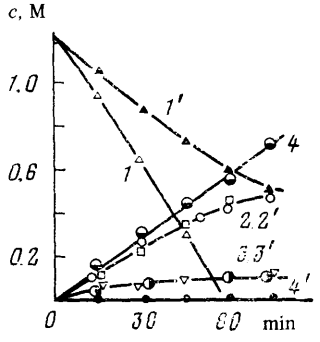


Figure 9. Kinetic curves for the consumption of styrene (curve *1*), the accumulation of benzaldehyde (curve *2*), styrene oxide (curve *3*), and the polymer (curve *4*) in the joint oxidation of styrene and acetaldehyde in benzene at 70 °C; the primed numerals denote the corresponding quantities in the presence of 2×10^{-5} M tanol. The end of the induction period was adopted as the starting point of the time readings[71].

A necessary condition for selective inhibition is the ability of the inhibitor to interact preferentially with one of the radicals of the chain. This can be achieved both by selecting an inhibitor and with markedly different constants for interaction with different types of radicals and by maintaining an optimum inhibitor concentration in the system. The calculation of the optimum inhibitor concentration range, based on the coupled oxidation mechanism given above and supplemented by elementary stages with participation of tanol (Im), i.e.

$$\dot{RCO} + \dot{Im} \rightarrow RCOIm, \quad (66)$$

$$\dot{M} + \dot{Im} \rightarrow MIm, \quad (67)$$

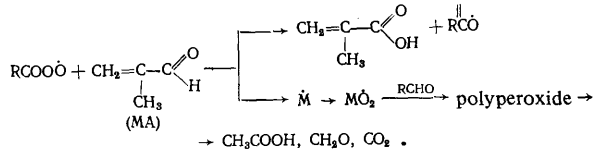
$$MIm\ (RCOIm) + MO_2^{\cdot}\ (RCOO^{\cdot}) \begin{cases} \rightarrow MO_2M + \dot{Im}, \\ \rightarrow \text{molecular products}, \end{cases}$$

$$MO_2^{\cdot} + MO_2^{\cdot} \rightarrow \text{molecular products}, \quad (68)$$

leads to the following condition for selective inhibition in the system[70]:

$$\frac{k_{66}k_{60}[O_2]}{k_{66}(k_{59}+k_{60})} > \dot{Im} > \frac{k''_{60}(w_i k_{68})^{1/2}[O_2]}{k'_{60}k_{67}[C_nH_{2n}]}. \quad (69)$$

The selective inhibition method has also been used to develop a new procedure for the synthesis of methacrylic acid (MAA) [73] by the liquid-phase oxidation of methacroleine (MA), which can be regarded as a coupled reaction involving two reaction centres of the same molecule:



The use of tanol as the inhibitor and of a heterogeneous catalyst (TiB_2) made it possible to devise a process with a selectivity of 84 mole % (with respect to the aldehyde which has reacted) for a degree of conversion of 40 mole % (Table 3).

Table 3. The influence of tanol (T) on the composition and yields of methacroleine oxidation products (70 °C; air pressure 25 atm; solvent—benzene; TiB_2 catalyst).[73]

Starting materials		Reaction time, h	Degree of conversion, mole %	[MAA]/Δ[MA], %	CH_3COOH/Δ[MA], %
[MA], M	10^5[T], M				
0.50 *	—	7	10	—	—
0.46 **	0.29	7	3.5	82.0	13.5
1.00 ***	1.16	3	41	84.0	16.0
1.00 ***	—	3	62	32.0	27.0

*In the absence of the catalyst.
**Catalyst at a concentration of 1.0 g litre^{-1}.
***Catalyst at a concentration of 2.5 g litre^{-1}.

4. Kinetics of Oxidation Reactions in Open Systems

The study of the kinetics of chemical reactions in open systems as a theoretical basis for continuous processes in chemical engineering has made a definite contribution to the solution of problems of the optimisation of technological processes. The results of studies of the kinetics of liquid-phase oxidation reactions of hydrocarbons in open systems are considered below. The complex radical chain oxidation mechanism can be represented by the following sequence of transformations:

$$\underset{\text{hydrocarbon}}{RH} \xrightarrow{k_I} \underset{\text{hydroperoxide}}{ROOH} \xrightarrow{k_{II}} \underset{\text{ketone}}{R'COR''} \xrightarrow{k_{III}} \underset{\text{acid}}{R'COOH}. \quad (70)$$

Here k_I, k_{II}, and k_{III} are the overall reaction constants representing sets of rate constants for elementary stages.

In a continuous process the substance RH to be oxidised is introduced into the reactor at a constant rate and part of the reacting mixture is removed. The attainment of steady-state concentrations of products is characteristic of reactions in open systems. The steady-state concentration of the final product is then higher the lower the specific rate# of

The specific rate ν is the volume of the initial liquid component supplied per unit time per unit volume of the reactor and has the dimension of reciprocal time.

supply of the starting materials ν.[75] For intermediates, for example, the hydroperoxide[75], this relation has an extremum (Fig.10) and, in conformity with the simplified mechanism (70), can be formulated thus:

$$\frac{d[ROOH]}{d\nu} = \frac{k_I[RH]_0(\nu^2 - k_I k_{II})}{(k_I+\nu)^2(k_{II}+\nu)^2} .$$

The rate of accumulation of all the oxidation products also passes through a maximum as a function of ν and the maximum rate of accumulation of the more extensive oxidation product is attained at lower flow rates ν. The maximum rate of accumulation of the final reaction product is attained at the same flow rate as the maximum steady-state concentration of the precursor. This property of an open system suggested a method for determining the pathways leading to the formation of the final reaction products[75]. It consists in comparing the positions of the maxima in the relations between the rates of accumulation of the final products and the steady-state concentrations of intermediates, on the one hand, and the flow rate, on the other. When these maxima are attained for the same flow rate, one can assume that the intermediate is a direct precursor of the given final product.

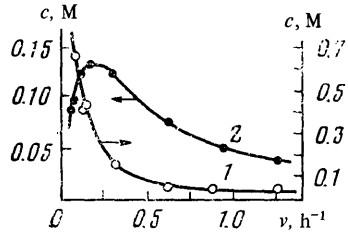


Figure 10. Dependence of the stationary concentrations of acids (curve *1*) and hydroperoxides (curve *2*) on the rate of supply of n-decane in the oxidation of the latter in an open system at 140 °C.[75]

A characteristic feature of reactions in open systems—the attainment of steady-state concentrations of the starting materials and reaction products—made it possible to develop a new kinetic method for the determination of the rate constants for the formation and consumption of intermediates in complex reactions involving free radicals. The method is based on the variation of the steady-state concentration of the intermediate, the rate of consumption of which is to be measured, keeping constant the steady-state concentration of free radicals. This is achieved by supplying into the reaction vessel initially the pure starting material and then its mixtures with the given product P at the same flow rate. Since ν remains constant, the steady-state concentrations of free radicals are the same in both cases. The effective rate constant $k_{2''}[RO_2]$ for the consumption of the product P can be calculated from the difference between the steady-state concentrations established when these solutions are introduced into the vessel, namely $[\bar{P}]$ and $[\bar{P}]_1$ respectively:

$$[P]_0/([\bar{P}]_1 - [\bar{P}]) = (1 + k_2'' [\dot{RO}_2]/\nu) ,$$

where $[P]_0$ is the concentration of P in the mixture entering the vessel.

This method has been used to determine the reactivity of products with respect to the radicals $\dot{RO}_2$ in the oxidation reactions of ethylbenzene and n-decane[28]. As an example, Fig.11 presents the steady-state concentrations of methylphenylmethanol and acetophenone for different contents of methylphenylmethanol in the ethylbenzene supplied to the vessel. The effective rate constant for the consumption of methylphenylmethanol ($k_{2''}$,ROH) was determined from the slope of the relation between $[\overline{ROH}]_1 - [\overline{ROH}]$ and $[ROH]_0$ (Fig.11, curve *4*). The reactivity of the $\dot{RO}_2$ radical with respect to the n-decane oxidation products was determined by the same method.

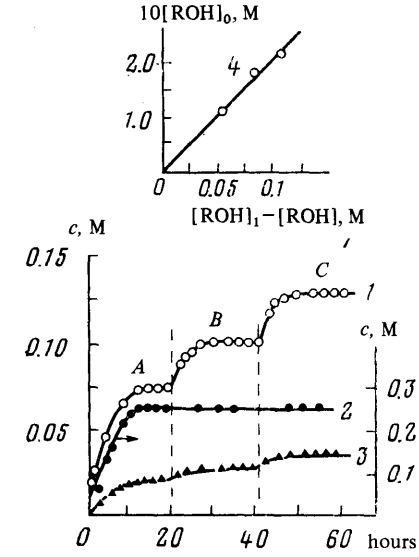


Figure 11. Kinetic curves for the accumulation of methylphenylmethanol (curve *1*), hydroperoxide (curve *2*), and acetophenone (curve *3*) in the oxidation of ethylbenzene in an open system with supply into the reaction vessel of ethylbenzene (*A*) and solutions of methylphenylmethanol in ethylbenzene containing 0.05 M (*B*) and 0.1 M (*C*) alcohol; ν = 0.215 h^{-1}; 4) dependence of the difference between the stationary concentrations of methylphenylmethanol on its concentration in ethylbenzene $[ROH]_0$; ν = 0.102 h^{-1}; 118 °C.[28]

If several isomers containing a functional group in different positions are formed in the reaction, the proposed method makes it possible to determine the rates of formation and consumption of each isomer separately without determining the concentrations of the individual isomers[77].

5. Catalysis of Oxidation

The most important method for increasing the rate and selectivity of oxidation involves the use of homogeneous and heterogeneous catalysts. Catalytic hydroperoxide oxidation and decomposition reactions as well as the problem of using catalysts to increase the selectivity of liquid-phase oxidation have been examined in detail recently in a number of reviews [78-81] and we shall therefore deal only very briefly with studies on catalysis.

The acceleration of liquid-phase oxidation processes by the addition of variable-valence metal compounds is associated with the participation of the catalysts in the chain branching

(radical decomposition of the hydroperoxide), chain initiation (activation of oxygen), and chain propagation stages. The decomposition of hydroperoxides, leading to the formation of free radicals, is the stage of the oxidation process involving the catalyst which has been studied in greatest detail. In most cases this reaction ensures the acceleration of the oxidation in the presence of both homogeneous[79] and heterogeneous[81] catalysts based on variable-valence metals.

The decomposition of hydroperoxides proceeds via an intermediate stage involving the formation of complexes between the catalyst and the hydroperoxide. To demonstrate this, a combination of kinetic and physicochemical (ultraviolet and infrared spectroscopy, NMR, EPR, etc.) methods for the quantitative investigation of catalyst–hydroperoxide systems under various conditions was used[82–84]. The simplest mechanism of the decomposition of a hydroperoxide, taking into account the formation of intermediate complexes between the catalyst and the hydroperoxide, is

$$n\,M^{n+} + m\,ROOH \rightleftarrows [n\,M^{n+} m\,ROOH] \rightarrow n\,M^{(n+1)+} + R\dot{O} + OH^- + (m-1)\,ROOH;$$

$$n_1 M^{(n+1)+} + m_1 ROOH \rightleftarrows [n_1 M^{(n+1)+} m_1 ROOH] \rightarrow$$

$$\rightarrow n_1 M^{n+} + R\dot{O}_2 + H^+ + (m_1 - 1)\,ROOH\ .$$

The quantities m, m_1, n, and n_1 depend on the nature of the catalyst and the hydroperoxide[83–85].

In the decomposition of the hydroperoxide in the presence of heterogeneous catalysts the process proceeds via a homogeneous-heterogeneous mechanism: the radicals formed in the decomposition of the hydroperoxide on the catalyst surface escape into space, where they can propagate the oxidation chain or recombine:

$$ROOH + S \begin{cases} \longrightarrow [ROOH \ldots S] \rightarrow R\dot{O} + [\dot{O}H \ldots S] \\ \longrightarrow [ROOH \ldots S] \rightarrow R\dot{O}_2 + [H \ldots S] \end{cases}.$$

This hydroperoxide decomposition mechanism has been demonstrated by the method of inhibitors[86] and by measuring the chemiluminescence of solutions[87] in the decomposition of cumenyl hydroperoxide in the presence of iron oxides.

The method proposed[89] for the investigation of the conductivities of transistor semiconducting structures has been used successfully to investigate complexes with partial charge transfer between the hydroperoxide and the heterogeneous catalyst. It makes it possible to identify the intermediate complexes and to determine their polarities and formation constants. The method is based on the change in the conductivity of the semiconducting triode structure of the type $p-n-p$ or $n-p-n$ following the adsorption of electron-donating and electron-accepting molecules. The adsorption of acceptors widens the base (the narrow middle band) in structures of the type $n-p-n$ and is accompanied by a decrease of conductivity. The adsorption of electron donors leads to an increase of n-type conductivity in the surface region of the base; for structures of the type $p-n-p$, donors and acceptors have the opposite effects.

The quantitative parameters of complex formation in the interaction of organic hydroperoxides with catalysts—copper and potassium hexacyanoferrates(III) and germanium oxide—have been obtained with the aid of this method[90]. The hexacyanoferrates(III) were deposited on the oxidised surface of a silicon structure of the $n-p-n$ type by adsorption from aqueous solutions. Fig.12 illustrates the variation of the conductivity $\Delta I/I_0$ of the structure with deposited hexacyanoferrates(III) (I_0 is the conductivity of the initial structure) under the influence of the adsorption of the hydroperoxide. It follows from the analysis of these curves that, in relation to both catalysts, α-phenylethyl hydroperoxide behaves as **an electron** donor. The limiting change in conductivity ΔI, observed when the catalyst surface is saturated with the hydroperoxide, is almost an order of magnitude higher for $Cu_3[Fe(CN)_6]_2$ than for $K_3[Fe(CN)_6]$. Thus the charge transferred from the hydroperoxide molecule to the first catalyst is much greater than for the second catalyst.

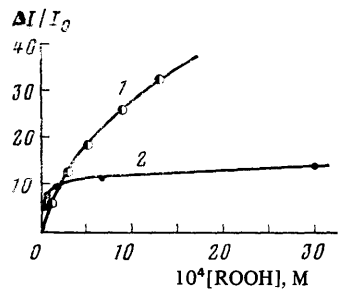


Figure 12. Variation of the conductivity of a transistor structure of the type $n-p-n$ with deposited metal hexacyanoferrates(III) as a function of the concentration of α-phenylethyl hydroperoxide in solution: 1) $Cu_3[Fe(CN)_6]_2$; 2) $K_3[Fe(CN)_6]$; solvent—heptane; 30 °C.[90]

The equilibrium constant for the formation of the complex of α-phenylethyl hydroperoxide with the catalyst, found from Fig.12 for $K_3[Fe(CN)_6]$, exceeds by a factor greater than 20 the equilibrium constant for $Cu_3[Fe(CN)_6]_2$ (Table 4).[90] It is significant that the equilibrium constant for the complex of the $Cu_3[Fe(CN)_6]_2$ catalyst with α-phenylethyl hydroperoxide, obtained by the method of transistor structures, virtually agrees with independent measurements of the same quantity by the kinetic method (5.5×10^2 litre mol^{-1}).[90] Table 4 also lists the parameters of the complex formation reactions of α-phenylethyl and t-butyl hydroperoxides with germanium oxide. In this case the activation of the hydroperoxide is associated with the transfer of an electron from the catalyst to the hydroperoxide.

Table 4. Physicochemical parameters of hydroperoxide–catalyst complexes (30 °C; solvent—heptane; gas phase—argon).[90]

Catalyst	α-Phenylethyl hydroperoxide		t-Butyl hydroperoxide		Cumenyl hydroperoxide	
	K, litre mol^{-1}	$\Delta I/I_0$	K, litre mol^{-1}	$\Delta I/I_0$	K, litre mol^{-1}	$\Delta I/I_0$
$Cu_3[Fe(CN)_6]_2$	$7.0 \cdot 10^2$	80.0	—	—	—	—
$K_3[Fe(CN)_6]$	$1.7 \cdot 10^4$	14.0	—	—	$1.4 \cdot 10^4$	3.0
Cu^{2+}/GeO_2	$7.7 \cdot 10^4$	10.0	—	—	—	—
Cu^{2+}/GeO_2 *	$6.1 \cdot 10^4$	18.5	$5.8 \cdot 10^3$	36.0	—	—
GeO_2	$3.0 \cdot 10^4$	4.5	—	—	—	—

*Gas phase—oxygen.

Comparison of the physicochemical characteristics of complexes of various hydroperoxides and heterogeneous catalysts with the activities of the catalysts in the hydroperoxide decomposition reaction shows that the highest rates of decomposition correspond to the formation of more polar and weaker reactant–catalyst bonds.

Together with the decomposition of the hydroperoxide, the formation of free radicals in the interaction of the catalyst with the starting materials—oxygen and the hydrocarbon (activation of oxygen and the hydrocarbon)—can play a major role in the presence of catalysts. The activation of oxygen apparently plays the main role in the initiation of the oxidation chain in the presence of catalysts. The possibility of the process via the mechanism

$$M^{n+} + O_2 \rightarrow M^{n+} \ldots O_2 ,$$
$$M^{n+} \ldots O_2 + RH \rightarrow M^{n+} + \dot{R} + H\dot{O}_2 ,$$

was first demonstrated by the method of inhibitors for the oxidation of ethylbenzene in the presence of nickel acetylacetonate[91] and was subsequently confirmed for a number of homogeneous and heterogeneous catalysts.

The activation of oxygen on the catalyst with subsequent increase of the rate of chain initiation apparently plays an important role in oxidation reactions in the presence of copper complexes of o-phenanthroline[92]. The study of the influence of oxygen on the rate of oxidation of cumene in the presence of copper complexes of o-phenanthroline at 30–40 °C demonstrated a strong dependence of the rate of oxidation on the oxygen pressure up to 760 mmHg [92] (Fig.13).

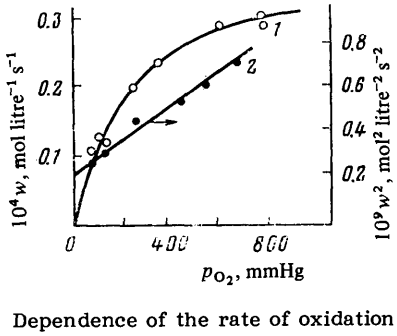


Figure 13. Dependence of the rate of oxidation of cumene in the presence of the complex $Cu(acac)_2$ with o-phenanthroline on the partial pressure of oxygen (curve *1*) and the transformed version of this relation (curve 2); 30 °C.[92]

The relation obtained can be readily explained by the involvement of the catalyst in the chain initiation reaction. Indeed the rate of oxidation of cumene should be described by the following equation in this case:

$$w = \frac{k_2}{k_6^{1/2}} [RH] \sqrt{w_0 + k' [O_2]} ,$$

which holds satisfactorily in the experiment (Fig.13). Furthermore, the rate of oxidation of cumene is in this case three times higher than the rate of oxidation calculated by the formula $w = (k_2^2/k_6)[RH]^2$, which takes into account the involvement of the catalyst only in chain branching.

The formation of charge-transfer complexes between $Rh(PPh_3)_3Cl$ and oxygen has been detected by EPR. In the presence of oxygen the diamagnetic catalyst species are converted into the complex $Rh(II).O_2^-$, in the EPR spectrum of which it is possible to identify groups of lines due to Rh(II) and O_2^- (Fig.14).[21] The role of these complexes in the oxidation process has been established by introducing into the systems certain specific additivies, which make it possible to increase the concentration of the oxygen complexes, the rate of oxidation increasing in the presence of such additives (Fig.14).

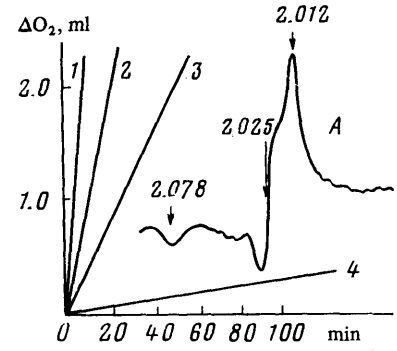


Figure 14. Kinetic curves for the absorption of O_2 in the oxidation of solutions of cyclohexene (line *1*), ethylbenzene (line *2*), and nonene (line *3*) in toluene in the presence of the modified complexes $Rh(PPh_3)_2COCl$ at 25 °C and kinetics of the absorption of O_2 by a solution of cyclohexane in the presence of the unmodified catalyst (line *4*). *A*) EPR spectrum of the modified catalyst at 77 K.

The activation of oxygen and the involvement of the catalyst in the chain initiation reaction are apparently largely responsible for the catalytic effect in the presence of variable valence metal oxides[93]. For a series of metal oxides, the initiating function in oxidation processes apparently reduces solely to their involvement in chain initiation. Thus the oxides ZnO, FeO, and NiO hardly decompose the hydroperoxide. In the presence of these catalysts virtually the only oxidation product is the hydroperoxide (Table 5).[93]

Table 5. The oxidation of cumene and the rate of decomposition of cumenyl hydroperoxide in the presence of metal oxides at 73 °C.[93]

Catalyst	Amount of catalyst, mg ml^{-1}	[ROOH], mole %	[DMPA], mole %	[AP], mole %	$10^2 w_{ROOH}$, mol litre^{-1} min^{-1}
MnO	0.10	54	17.0	2.0	100
Co_2O_3	2.50	52	16.0	1.6	55
Fe_2O_3	2.50	78	10.0	1.2	24
FeO	30.0	90	3.0	0.25	2
NiO	1.5	87	4.2	0.13	2
Cr_2O_3	2.5	89	2.0	0.1	0.5
ZnO	20.0	96	2.0	0.1	0
Bi_2O_3	10.0	90	2.0	0.1	0

[It is not clear from the context what DMPA and AP are (Ed. of Translation)].

To increase the rate and selectivity of the liquid-phase oxidation of organic compounds in the presence of homogeneous and heterogeneous catalysts, the principle of the donor–acceptor modification of these catalysts is used[94]. Thus the selectivity of the oxidation of isopropylbenzene to the hydroperoxide can be increased from 82 to 92% (relative to the absorbed oxygen) with the aid of the preliminary

adsorption of carbon dioxide or dicyanomethylene-2,4,7-trinitrofluorenone [DTF] on the surface of the heterogeneous catalyst (AgO).[94] Electron-donating modifying agents (CO, NH_3) increase in this process the rate of oxidation and the rate of accumulation of the product (alcohol), while electron-accepting modifying agents (CO_2, DTF) decrease the rate of oxidation and ensure a high process selectivity with respect to the hydroperoxide.

An example of the modifying effect of solid additives is provided by the oxidation of ethylbenzene on silver catalysts containing 0.02 at.% of various metals (Ca, Mo, Cl, Bi, and Co).[95] The catalyst may be modified in the course of the oxidation process itself as a result of the accumulation of certain reaction products. Thus, in the liquid-phase oxidation of tetralin in the presence of the Ag_2O catalyst deposited on SiO_2 (Fig.15),[96] the composition of the products initially agrees with the composition of the products of the non-catalysed oxidation: the three main reaction products (tetralyl hydroperoxide, 1-tetralol, and 1-tetralone) accumulate at comparable rates. As the process develops, the accumulation of the ketone and alcohol stops completely and the only reaction product becomes the hydroperoxide, i.e. the catalyst is modified with participation of oxygen-containing products. The modified catalyst ensures the inhibition of the chain reaction and can activate molecular oxygen.

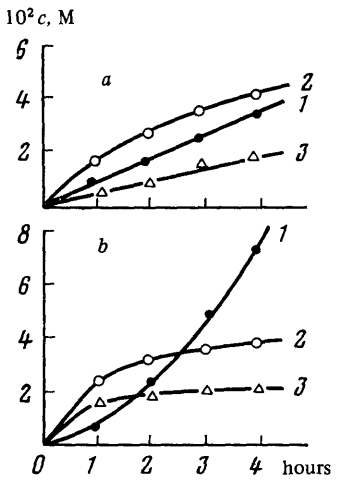


Figure 15. Kinetic curves for the accumulation of tetralyl hydroperoxide (curve *1*), 1-tetralone (curve *2*), and 1-tetralol (curve *3*) in the oxidation of tetralin: *a*) without catalyst; *b*) in the presence of 0.4 g litre^{-1} of deposited heterogeneous catalyst; 130 °C.[96]

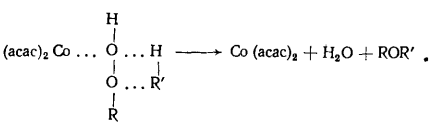
The efficiency of the donor–acceptor modification when homogeneous catalysts are used has been demonstrated in relation to the oxidation of ethylbenzene in the presence of nickel bis(acetylacetonate) [97] and the oxidation of cyclohexane catalysed by the rhodium complex $Rh(PPh_3)_3Cl$.[98]

The decomposition of the hydroperoxide without the formation of free radicals (molecular decomposition of the hydroperoxide) can play an important role in the mechanism of the catalytic oxidation of hydrocarbons and other organic compounds. Such decomposition can lead to the formation of new products uncharacteristic of the non-catalytic oxidation. On the other hand, the intense molecular decomposition of the hydroperoxide, which is an important source of free radicals, can lead to the inhibition of the oxidation process.

Direct evidence for the molecular pathway leading to the decomposition of the hydroperoxide in the presence of the catalyst has been obtained with the aid of the method of inhibitors in relation to the decomposition of n-decyl hydroperoxide in the presence of copper stearate[85]. The considerable (up to 90%) molecular decomposition of the hydroperoxide is characteristic of the decomposition of tetralinyl hydroperoxide in the presence of cobalt stearate[99].

The study of the dependence of the rate of decomposition of the hydroperoxide and of the consumption of the inhibitor (radical decomposition) on the catalyst and hydroperoxide concentrations established that both decomposition pathways proceed via the formation of the same complex[100,101]. The "cage effect" of the solvent plays an important role in the molecular mechanism of the decomposition of the hydroperoxide[102]. The radicals formed in the decomposition of the complex $M^{n+}.ROOH$ can either recombine in the solvent cage (molecular decomposition of the hydroperoxide) or can diffuse from the cage (radical decomposition). The ratio of the radical and molecular hydroperoxide decomposition pathways depends greatly on the viscosity of the medium (η): with increase of η, the contribution of the molecular decomposition of ROOH increases. The molecular decomposition of the hydroperoxide in the presence of heterogeneous catalysts takes place via an analogous mechanism[98].

In the non-catalytic decomposition of the hydroperoxide, the involvement of solvent molecules [reaction (3′)] in the process leads to an increase of the rate of formation of free radicals. In the presence of the catalyst the addition of organic solvents with a mobile C–H bond acclerates the molecular decomposition[98,102]. Thus, in the decomposition of cumenyl hydroperoxide in the presence of $Co(acac)_2$, the rate of decomposition of the hydroperoxide is almost independent of the concentration and nature of the solvent. The contribution by the molecular decomposition increases greatly with increase of the hydrocarbon concentration in the solvent and to a greater extent the smaller the C–H bond strength in the hydrocarbon[102], which is apparently associated with the interaction of RH with the hydroperoxide activated by the partial electron transfer to the catalyst–ROOH complex:



The decomposition of t-butyl hydroperoxide in the presence of oxide catalysts is significantly inhibited by the addition of hydrocarbons with a mobile C–H bond. A change in the composition of the reaction products is then observed—the accumulation of a new product, namely an asymmetric hydroperoxide containing the t-butyl group and the alkyl group forming part of the composition of the solvent. The hydroperoxide decomposes in this case without the release of free radicals into space and is apparently a "concerted" process (simultaneously dissociated of the bonds in the starting materials and the formation of new bonds in the hydroperoxides).

The catalytic oxidation of organic compounds in alkaline media by molecular oxygen is apparently a promising reaction[103–105]. Copper complexes of *o*-phenanthroline and bipyridyl can serve as catalysts in such systems. Alcohol and ketones capable of forming ions in alkaline media are oxidised. The rate of oxidation of these substances is

independent of the nature of the base and increases with increase of the pH of the medium in the pH range from 10 to 12 (Fig.16). At pH > 12 the rate of oxidation falls owing to the deactivation of the catalyst.

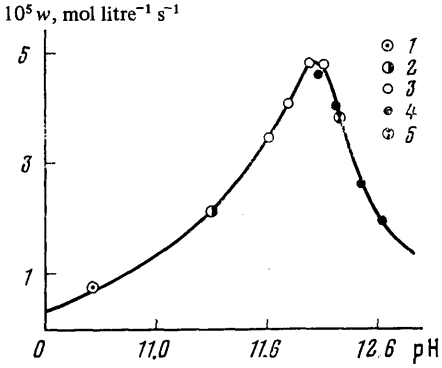


Figure 16. Dependence of the rate of oxidation of ethyl methyl ketone (EMK) on the pH of the medium in the presence of various bases: 1) $Mg(OH)_2$; 2) Na_2CO_3; 3) $(C_2H_5)_3N$; 4) NaOH; 5) $Ca(OH)_2$; 10 ml H_2O, 0.5 ml EMK; $[CuCl_2]_0 = 5 \times 10^{-3}$ M; $[o\text{-phen}]_0 = 1.5 \times 10^{-2}$ M; 50 °C.[92]

The alkali + $CuCl_2$ + *o*-phenanthroline catalytic system is capable of ensuring at pH > 9 rates of oxidation of alcohols and ketones up to 50–80 mole % per hour and more (at 30° to 50 °C), which are virtually unattainable in the catalytic oxidation of organic substrates in neutral media.

The main products of the oxidation of alcohols and ketones, i.e. acids, are the primary reaction products under the conditions of alkaline oxidation. The anions are the active form of the substrate. The strong influence of the medium on the electron-donating capacity of the anions makes it possible to alter the rate of the process and the selectivity of the oxidation by changing the solvent. Thus the rate of oxidation of a 40% solution of methanol in benzene is almost an order of magnitude higher than the rate of oxidation of methanol in bulk. The oxidation apparently develops via a non-chain mechanism without the release of free radicals into space and proceeds as a result of the interaction of O_2 with the anion A^- activated by its incorporation in the complex $Cat.A^-$ with the catalyst.

In the general form, the oxidation mechanism consists of a sequence of the following stages[106]:

$$Cu^{2+} + R'\overline{C}HC(O)R'' \rightleftarrows Cu^{2+} \cdot R'\overset{\ominus}{C}HC(O)R'',$$

$$Cu^{2+} \cdot R\overline{C}HC(O)R'' + O_2 \rightarrow Cu^{+} + R'C\begin{matrix}O\\ \diagdown\\ OH\end{matrix} + R''C\begin{matrix}O\\ \diagdown\\ OH\end{matrix},$$

$$Cu^{+} + R'\overline{C}HC(O)R'' \rightleftarrows Cu^{+} \cdot R'CHC(O)R''$$

$$Cu^{+} \cdot R'\overline{C}HC(O)R'' + O_2 \rightarrow Cu^{2+} + R'C\begin{matrix}O\\ \diagdown\\ OH\end{matrix} + R''C\begin{matrix}O\\ \diagdown\\ OH\end{matrix},$$

In the oxidation of ketones the interaction of the coordinated anion with O_2 proceeds at very high rates and does not limit the rate of oxidation. In the oxidation of alcohols oxygen participates in the rate-limiting stage of the process and in this case the rate of oxidation greatly depends on the oxygen pressure[104].

6. Metal Complex Inhibition

Approximately three decades ago, the phenomenon of the dual function[107] of variable-valence metal compounds in liquid-phase oxidation reactions was discovered. It consists in the fact that, with increase of the initial concentration of the metal complexes, there is a sharp (critical) change in the rate of reaction—a transition from the catalytic to inhibited oxidation conditions. Recently there has been a considerable growth of interest in the use of metal complexes as inhibitors of liquid-phase oxidation and in the study of the mechanism of the metal complex inhibition.

The inhibition of oxidation in the presence of metal compounds is due to two causes: the decomposition of the hydroperoxide into non-radical products and the interaction of free radicals with metal complexes. The latter type of inhibition is most common. The mechanisms of the reactions of $R\dot{O}_2$ radicals with metal compounds, leading to the termination of oxidation chains, are considered below.

The inhibition by the sulphur-containing metal complexes, namely bis(dialkyl phosphorodithioates) $[M(dtp)_n]$,[111–118] bis(*N*,*N*-dialkyldithiocarbamates) $[M(dtc)_2]$,[109–115] bis(8-mercaptoquinolinates) $[M(toq)_n]$,[119] and bis(α-thiopicolinanilides) $[M(tpa)_2]$ [108,109] takes place as a result of chain termination by the complexes. The stoichiometric inhibition coefficient *f* and the rate constant for the reaction of $R\dot{O}_2$ with the metal complexes depend greatly on the decomposition of the chelate unit, the nature of the metal, the coordinating atoms of the ligand, and the oxidation potential of the complex and its geometry (Table 6).

Table 6. Dependence of the effectiveness of inhibition (fk_7) by sulphur-containing complexes on the oxidation potentials ($E_{1/2}$) (oxidation of ethylbenzene; 75 °C; initiator—azobisisobutyronitrile; $w_i = 1 \times 10^{-6}$ mol litre^{-1} s^{-1}).[119]

Compound	$10^{-3}kf_7$, litre mol^{-1} s^{-1}	$+E_{1/2}$, V
	$M(toq)_n$	
$Zn(toq)_2$	2.3	1.10
$Ag(S\text{-}toq)$	1.3	0.93
$Co(S\text{-}toq)_3$	11	0.59
$Ni(S\text{-}toq)_2$	7.5	0.56
$Cu(toq)_2$	>60	0.48
	$M(dtc)_n$	
$Zn(dtc)_2$	1.6	1.01
$Bi(dtc)_3$	5.7	0.86
$Pb(dtc)_2$	6.3	0.80
$Ni(dtc)_2$	23	0.60
$Cu(dtc)_2$	60	0.43
	$M(tpa)_2$	
$Ni(tpa)_2$	2.6	0.88
$Cu(tpa)_2$	13	0.75

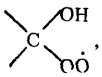
Table 6 shows that the inhibiting activity of the metal complexes is higher the greater the ease of oxidation of the complex[109,119]. An increase of the degree of covalence of the metal–ligand bond in the complex also promotes an increase of its inhibiting activity in the oxidation reaction[120]. The mechanism of the inhibition includes in this case the formation of a complex of $R\dot{O}_2$ with the chelate and subsequent electron transfer to the peroxy-radical[121]. The central metal ion plays the role of an agent transferring an electron to the peroxy-radical from the ligand, which is also split off in the

form of a radical incapable of participating in the chain propagation reaction. The degree of oxidation of the metal remains unchanged.

For $M(dtc)_2$, the reaction mechanism can be formulated as follows[109,110]:

$$M(dtc)_2 + R\dot{O}_2 \rightleftarrows \{M(dtc)_2 \ldots R\dot{O}_2\} \rightarrow \{[M(dtc)_2]^+ \ldots RO_2^-\},$$
$$\{[M(dtc)_2]^+ \ldots RO_2^-\} \rightarrow M(dtc)RO_2 + 2dt\dot{c},$$
$$2dt\dot{c} \rightarrow \text{disulphide}.$$

An analogous mechanism has been proposed for the inhibition of oxidation by the copper(I) complexes of triphenyl phosphite[122] as well as a number of phosphorodiothioates[115–118].

The electron transfer reaction between $R\dot{O}_2$ and the metal compounds can lead in some cases to a change in the oxidation state of the metal ion. Thus the oxidation of the Co^{2+} and Mn^{2+} ions has been observed in the interaction with radicals[123,124]. The phenomenon of repeated chain termination by metal ions has been observed in the oxidation of cyclohexanol and other secondary alcohols as well as amides in the presence of salts and certain complexes of copper, iron, cobalt, magnesium, and cerium[125]. This phenomenon is due to the fact that the hydroxyperoxy-radicals  , formed in the oxidation of secondary alcohols, can interact with metal ions in both valence states:

$$\rangle C(OH)O\dot{O} + Cu^{2+} \rightarrow H^+ + Cu^+ + O_2 + \rangle C{=}O,$$
$$\rangle C(OH)O\dot{O} + Cu^+ \rightarrow \rangle C(OH)OO^- + Cu^{2+}.$$

In this system the quantity f may increase to 10^3.

The oxidation-reduction potential of the metal ion is very important for the operation of the mechanism presented above. At high oxidation-reduction potentials the degree of involvement of the metal in the decomposition of the hydroperoxide increases; at low oxidation-reduction potentials the rate of reaction of M^{n+} with $R\dot{O}_2$ falls.

For certain types of metal complex inhibitors, the interaction with peroxy-radicals takes place via a mechanism involving the abstraction of a hydrogen atom from the ligand. The inhibition of the oxidation of cumene and cyclohexa-1,3-diene by cobalt(III) complexes [as well as iron(II), nickel(II), and copper(II) complexes] with dimethylglyoxime and other dioximes[126,127] and also by nickel bis(α-phenylanthranilate) apparently involves this mechanism[128].

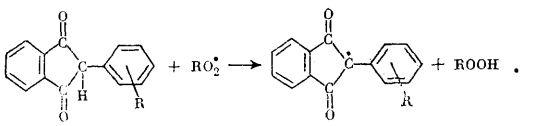
A hydrogen atom is abstracted from the ligand in the complex much more readily than from the free ligand, which indicates the activation of the ligand in the complex. Thus $k_{12} = 9 \times 10^2$ litre mol^{-1} s^{-1} (at 90 °C) for *N*-phenylanthranilic acid in ethylbenzene, while $k_{12} = 4.5 \times 10^3$ litre mol^{-1} s^{-1} for the nickel complex of *N*-phenylanthranilic acid[128].

7. The Mechanism of the Inhibited Oxidation

The study of the mechanism of the action of inhibitors and the establishment of theoretical principles for the selection of effective antioxidant additives is an important task in chemical kinetics. New classes of antioxidants have been investigated, rapid methods for the estimation of their efficiency have been proposed, and the details of the elementary stages of the inhibition process have been determined in recent years. Many fundamental results have been obtained with the aid of modern physical research methods—the chemiluminescence method, EPR, NMR, flash photolysis, and chemically induced nuclear polarisation (CINP).

The oxidation process is usually inhibited by adding to the system inhibitors which interact with free radicals and terminate oxidation chains[129]. The most common inhibitors of this type are phenols and aromatic amines. They cause chain termination via reaction (7).

Together with amines and phenols, 2-arylindan-1,3-diones, which have a reactive C–H bond, also serve as inhibitors[130]:



The constants k_7 for these inhibitors depend on the substituent in the benzene ring and amount to 1×10^2–6×10^4 litre mol^{-1} s^{-1} (Table 7). The substituents in the *p*-position, both electron-donating and electron-accepting, increase k_7, while those in the *o*-position decrease it. The influence of *p*-substituents is described by the Hammett equation in the form[131]

$$\lg(k_7/k_{7,\,st}) = 0.28\sigma + 1.01E_R.$$

Table 7. The rate constants, activation energies, and stoichiometric coefficients (f) for the reactions of cumenylperoxy-radicals with 2-arylindan-1,3-diones at 60 °C.[131]

R*	$10^{-4}k_7$, litre mol^{-1} s^{-1}	f	E_{act}, kcal mol^{-1}
	1.95	1.0	7.3
p-Br	2.9	1.7	5.0
p-Cl	2.8	1.2	6.0
p-N(CH$_3$)$_2$	2.25	2.0	5.0
p-OCH$_3$	2.0	1.8	5.5
o-OCH$_3$, *p*-OCH$_3$	0.12	—	—
o-OCH$_3$, *p*-OCH$_3$	0.01	—	—
p-CH$_3$	1.60	1.6	7.8
o-CH$_3$	0.09	—	—
β-Naphthyl	2.5	1.8	5.5
α-Naphthyl	0.88	1.0	9.5
Ionol	0.89	2.0	5.3

*Substituent in the 2-diphenyl[2-phenyl?] ring.

The subscript st refers to the unsubstituted 2-phenylindan-1,3-dione and σ and E_R are the polar and resonance constants of the substituents.

Together with reaction (7), there is also a possibility of recombination inhibition mechanisms. A new example of an inhibitor of this type is 1,2-bis(*p*-dimethylaminophenyl-1,2-diphthaloylethane)(PP). The inhibiting activity of PP is due to the equilbirium

$$PP \underset{k(-)}{\overset{k(+)}{\rightleftarrows}} 2\dot{P} \qquad (71)$$

and the irreversible reaction

$$R\dot{O}_2 + \dot{P} \rightarrow \text{products}. \qquad (72)$$

The radical P has been detected by EPR. The equilibrium constant is $k_{71} = 6.16 \times 10^2 \exp(-17\,300/RT)$ mol litre^{-1}, the rate constant for the recombination of $\dot{P}$ radicals at 20 °C is $k_{(a)} = 2 \times 10^8$ litre mol^{-1} s^{-1} and $k_{72} \geq 10^8$ litre mol^{-1} s^{-1}.[133]

The question of reactivity with respect to alkyl radicals is important for the mechanism of the action of inhibitors:

$$InH + \dot{R} \rightarrow \dot{In} + RH, \qquad (7')$$

$$\dot{R} + \dot{R} \rightarrow \text{products}. \qquad (73)$$

Estimates of the parameter $k_7'/k_{73}^{1/2}$ for the interaction of 16 inhibitors (amines and phenols) with alkyl radicals derived from ethhlbenzene showed[137] that its maximum possible value is $(0.4–3.5) \times 10^{-1}$ litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$. For $k_{73} = 2.8 \times 10^8$ litre mol^{-1} s^{-1}, we have $k_7' < (1–6) \times 10^3$ litre mol^{-1} s^{-1}. For *N*-phenyl-β-naphthylamine, $k_7'/k_{73}^{1/2} = (3.2 \pm 0.2) \times 10^{-2}$ litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$ and $k_7' = 6.7 \times 10^2$ litre mol^{-1} s^{-1}.

Thus phenols and aromatic amines interact with alkyl radicals much less vigorously than with peroxy-radicals, for which as a rule $k_7 \cong 10^4–10^5$ litre mol^{-1} s^{-1}.

The stable aliphatic nitroxy-radicals are effective acceptors of alkyl radicals[135]:

$$>\dot{N}O + \dot{R} \rightarrow NOR \quad . \qquad (74)$$

Aromatic nitroxy-radicals, which are capable of reacting with both the radicals $\dot{R}$ and $R\dot{O}_2$, act less selectively. Repeated chain termination in the oxidation of certain unsaturated hydrocarbons[137] and polypropylene[138] has been demonstrated for both types of nitroxy-radicals, apparently as a result of the regeneration of $>\dot{N}O$ when the ether derivatives of aliphatic nitroxy-radicals $>NOR$ interact with peroxy- and alkoxy-radicals and with oxygen[136]:

$$>NOR + R\dot{O}_2\ (R\dot{O},\ O_2) \rightarrow >N\dot{O} + \text{product}.$$

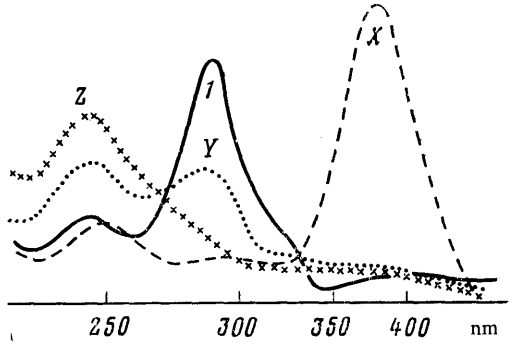
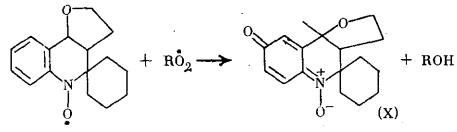


Figure 17. Ultraviolet absorption spectra of the 4-methyl-2-spiro-cyclohexyl-3,4,2',3'-tetrahydrofurano-1,2,3,4-tetraquinolin-1-yloxy-radical (curve *1*) and its reaction products (curves *X*, *Y*, and *Z*). Solvent—ethanol; [AIBN] = 4.9×10^{-2} M; $[N\dot{O}]_0 = 5.2 \times 10^{-4}$ M; 60 °C. Spectra *X* and *Z* were obtained in oxygen and spectrum *Y* was obtained in nitrogen[139].

Repeated chain termination in the inhibition by the aromatic 4-methyl-2-spirocyclohexyl-3,4,2',3'-tetrahydrofurano-1,2,3,4-tetrahydroquinolin-1-yloxy-radical of the oxidation of β-carotene[139] is due to a relay of radical reactions of the nitroxy-radical and its conversion products (Fig.17), which interact alternately with peroxy- and alkyl-radicals. The first stage involves the reaction of $>N\dot{O}$ with the radicals $R\dot{O}_2$:



The resulting quinone-nitrone (X) is an acceptor of the radicals $\dot{R}$:

$$X + 2\dot{R} \rightarrow Y; \quad Y + R\dot{O}_2 \rightarrow Z \quad .$$

The product Y then reacts with $R\dot{O}_2$.

As a result of the sequence of these reactions, five chains are terminated by the $>N\dot{O}$ fragment.

The radicals $\dot{In}$ formed in the interaction of InH with $R\dot{O}_2$ via reaction (7) interact with peroxy-radicals to form recombination products—quinolide peroxides (QP) [reaction (8)].

The values of k_8 for phenoxy-radicals depend little on the structure of $\dot{In}$ and $R\dot{O}_2$ and are in the range $(1.7–7.2) \times 10^8$ litre mol^{-1} s^{-1} (at 60 °C).[140–142] The probability α of the formation of QP depends on the concentration of the phenol, the rate of initiation, the rate constants k_7 and k_8, and the rate constant for the reaction

$$\dot{In} + \dot{In} \rightarrow \text{products}, \qquad (75)$$

and is defined by the equation[143]

$$\alpha^2(1+\alpha) - \frac{A}{k_9}(1-\alpha) = 0;$$

$$A = \frac{k_8^2 w_i}{k_7^2 [InH]^3} \quad .$$

Quinolide peroxides are formed with the highest probability ($\alpha = 1$) in inhibition by sterically hindered phenols whose phenoxy-radicals are stable and whose constants k_{75} are low. In the oxidation of low-molecular-weight hydrocarbons[144] in the presence of 2,4,6-tri-t-butylphenyl the yield of quinolide peroxide reaches 100%. Under the conditions of the inhibited oxidation, quinolide peroxides are capable of decomposing into radicals[143].

The initiating capacity of quinolide peroxides is comparable to that of azobisisobutyronitrile and benzoyl peroxide and is greatly superior to that of t-butyl hydroperoxide (Table 8).[143,144] The probability of the emergence of radicals from the cage in the decomposition of quinolide peroxides is close to unity. Their decomposition leads to a decrease of the antioxidant effectiveness of sterically hindered phenols in the autoxidation of hydrocarbons and polymers[143].

Table 8. Kinetic parameters of the thermal decomposition of quinolide peroxides (QP) [In = 2,4,6-tri-t-butylperoxy-radical, R = $C(CH_3)_3$] and certain initiators[143].

Compound	Decomposition rate constant, s^{-1}	$10^5 k$, s^{-1}
o-QP	$1.1 \cdot 10^{14} \exp[(-30500 \pm 1000)/RT]$	6.6
p-QP	$9.8 \cdot 10^{13} \exp[(-33000 \pm 2000)/RT]$	0.18
Azobisisobutyronitrile	$1.6 \cdot 10^{15} \exp(-30800/RT)$	57
Benzoyl peroxide	$3.0 \cdot 10^{14} \exp(-30800/RT)$	11
$(CH_3)_3COOH$	$3.6 \cdot 10^{12} \exp(-33000/RT)$	0.006

*At 93 °C.

Extensive information about the kinetics of reaction (75) for phenoxy-radicals has been obtained by flash photolysis[145–148]. The process mechanism can be represented by the following set of stages:

$$Ph\dot{O} + Ph\dot{O} \rightarrow D \quad , \qquad (76)$$

$$D \rightarrow Ph\dot{O} + Ph\dot{O} \quad , \qquad (77)$$

$$D \rightarrow \text{products}. \qquad (78)$$

The stage involving the irreversible transformation of the dimer [Eqn.(78)] is characteristic of radicals having at least one unoccupied *o*- or *p*-position. In this stage there is a possibility of the regeneration of the inhibitor. For the majority of phenoxy-radicals, $k_{76} \cong 10^9$–10^7 litre mol^{-1} s^{-1}.[148] The introduction of bulky substituents into the *p*-position relative to the O–H group causes a decrease of k_{76}. For example, the rate constant for the recombination of "galvinoxyl" radicals at 90 °C is 4.8×10^4 litre mol^{-1} s^{-1}.[149] The comparatively slow recombination of sterically hindered phenoxy-radicals is limited by molecular mobility. The cause of this effect consists in the low value of the steric factor for the interaction of these radicals[145].

The kinetic characteristics of the side processes involving inhibitors, i.e. the reactions of the inhibitor and its radicals with the hydrocarbon, the hydroperoxide, and oxygen, have been obtained. The kinetic parameters k_{79}/k_8, characterising the participation of the radical of *N*-phenyl-β-naphthylamine in the chain propagation reaction with a hydrocarbon (ethylbenzene), i.e.

$$\dot{\text{In}} + \text{RH} \rightarrow \text{InH} + \dot{\text{R}}, \qquad (79)$$

measured by the chemiluminescence method, is 3×10^{-9}.[150]

The rate constants for the reaction

$$\dot{\text{In}} + \text{ROOH} \rightarrow \text{InH} + \text{R}\dot{\text{O}}_2, \qquad (80)$$

involving t-butyl hydroperoxide and 2,6-di-t-butyl-4-R-phenols increase with increasing strength of the O–H bond in the phenol (the activation energy then falls). Thus, on passing from R = OCH_3 (D_{OH} = 73.9 kcal mol^{-1}) to R′ = CN (D_{OH} = 81.9 kcal mol^{-1}), the values of k_{80} at 60 °C increase from 0.07 to 170 litre mol^{-1} s^{-1} and the activation energy falls from 18 to 8.8 kcal mol^{-1}.

The formation of phenoxy-radicals in the reaction of a hydroperoxide with phenols[151],

$$\text{InH} + \text{ROOH} \begin{cases} \rightarrow \text{molecular products}, \\ \rightarrow \text{R}\dot{\text{O}} + \text{Ph}\dot{\text{O}} + \text{H}_2\text{O}, \end{cases} \qquad (81)$$

has been demonstrated by EPR for 2,4,6-tri-t-butylphenol. The constant k_{81} depends strongly on the structure of the phenol. For the interaction of cumenyl hydroperoxide with 2,6-dimethoxyphenol at 140, $k_{81} = 6.5 \times 10^{-3}$ litre mol^{-1} s^{-1} has been found, while the constant for the reaction with the sterically hindered 2,4,6-tri-t-butylphenol is $k_{81} = 7.5 \times 10^{-5}$ litre mol^{-1} s^{-1}.

It has been shown[152] that the reaction of aromatic amines, phenols, and naphthols with molecular oxygen,

$$\text{InH} + \text{O}_2 \rightarrow \dot{\text{In}} + \text{H}\dot{\text{O}}_2,$$

requires an activation energy of 25–35 kcal mol^{-1}. The contribution of this reaction to the initiation of the oxidation must be taken into account only above 180 °C and at high oxygen pressures.

For a long time, the question of the mechanism of the interaction of phosphites with a hydroperoxide [reaction (7‴)] remained controversial. The yield of radicals in this reaction is very low[154]. It was suggested that the reaction is either limited via a cryptoradical mechanism, with a low degree of liberation of radicals into space, or that two reactions take place in the system, involving radical and non-radical decomposition. Since the reaction products are the same in both cases, it was not possible to determine which of the two alternative mechanisms operates. It has been demonstrated unambiguously with the aid of CINP [153] that the reaction proceeds via two competing channels—radical and non-radical. The radical pathway, induced by the polarisation of the ^{31}P nuclei, makes an extremely small contribution (10^{-2} to 10^{-4} of the overall decomposition).

A special method using computers—an automatic system for testing inhibitors (ASTI), which takes into account the set of elementary stages in the action of inhibitors in the oxidation process—has been recently developed and introduced (Fig.18). Tests are performed simultaneously on four highly sensitive differential manometric sets of apparatus, with automatic recording of the rate of oxidation, located in the experimental section. The experimental data are transmitted to the intermediate memory of the computer—an autonomous accumulator on a magnetic drum (section B). Sections A and B are linked by a communication line. On command of the experimentor, the data are introduced into the computer for treatment; the results of the computation are transmitted to the laboratory and are reproduced in the form of tables and graphs with the aid of a graph plotting apparatus.

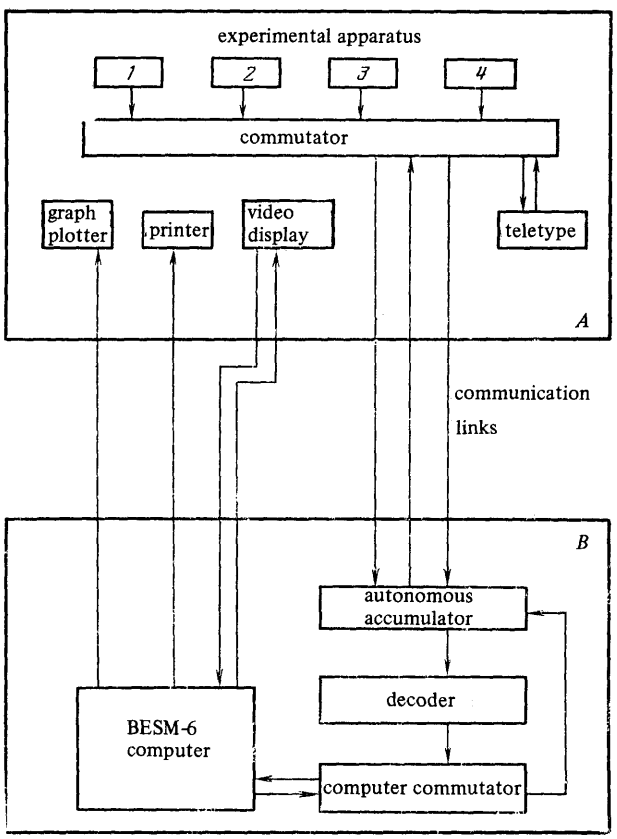


Figure 18. Schematic illustration of the automated system for testing the efficiency of stabilisers (ASTI): *A*) experimental section; *B*) section for the interpretation of data.

8. Synergism

The effects of synergism, which is manifested by the fact that the inhibiting effect of a mixture of two inhibitors exceeds the sum of the effects of each separately, is of practical importance. The mechanism of the synergism in the inhibition of oxidation by a mixture of inhibitors, each of which reacts with the radicals $\text{R}\dot{\text{O}}_2$, has been most thoroughly

investigated. The mechanism of the action of a mixture of inhibitors includes, together with the main elementary stages of the inhibited oxidation process [reactions (0), (2), (3), and (6)–(8)], also the following reactions[155–157]

$$In_1^{\cdot} + RH \rightarrow In_1H + \dot{R}\,(R\dot{O}_2)\,, \qquad (82)$$

$$In_1^{\cdot} + In_2H \rightarrow In_1H + In_2^{\cdot}\,, \qquad (83)$$

$$In_2^{\cdot} + In_1H \rightarrow In_2H + In_1^{\cdot}\,. \qquad (84)$$

The synergism is based on the phenomenon of the radical interaction of the inhibitors[155–158] consisting in the reduction of the more active inhibitor In_1H as a result of the transfer of a hydrogen atom to the radical $In_1^{\cdot}$ from the molecule of the less active inhibitor In_2H [reaction (83)]. The inhibitors In_1H can be primary and secondary aromatic amines, substituted pphenylenediamines, hydroxylamine ethers, and sterically unhindered alkylphenols[159]. The reducing inhibitors can be phenols and bisphenols containing bulky substituents in the 2,6-positions. The effective reduction of In_1H occurs only when the radical $In_2^{\cdot}$ formed is inactive and does not enter into the reversible reaction (84).

The influence of reaction (83) on inhibition by mixtures is enhanced due to the suppression, as a result of its occurrence, of reaction (79), which lowers the inhibiting activity of aromatic amines and unshielded phenols.

It has been shown by computer calculations that this mechanism describes satisfactorily the dependence of the synergistic effect on the overall concentration of inhibitors[160], the kinetic characteristics of the substrate being oxidised[156], the efficiency of the action of each inhibitor in the mixture[156,157], and the mixture composition[161]. For mixtures of the same inhibitor In_2H with inhibitors In_1H having the different antiradical activities, the synergistic effect increases with increase of the rate constant for the reaction of $R\dot{O}_2$ with In_1H and the maximum on the plot of the dependence of τ on the mixture composition shifts in the direction of mixtures containing a higher percentage of In_2H.[161]

A similar mechanism of the regeneration of the inhibitor explains in many instances the synergistic effect of a mixture of aromatic amines and sulphur-containing compounds, for example, mixtures of *N*-phenyl-β-naphthylamine and bis(2-hydroxy-5-methyl-3-t-butyl) sulphoxide[162]. The product of the thermal transformation of the sulphoxide (P) behaves as the reductant for the amine. The same mechanism is possible in inhibition by mixtures containing sulphides, where the product P can be obtained by the reaction of the sulphides with the hydroperoxide and subsequent decomposition of the resulting sulphoxide. The synergistic effect of a mixture of copper and nickel bis(*N*,*N*'-diethyldithiocarbamates) with thiuram disulphide—the product of the reaction of these complexes in liquid-phase oxidation—is due to the regeneration of the initial form of the metal-complex inhibitor $M(dtc)_2$.[163]

Together with the mechanism of the synergism discussed above, which is due to the regeneration of the active inhibitor, cases are possible where the synergism is due to the formation of a new active inhibitor in the system. This apparently happens in the inhibition of oxidation by mixtures of aromatic amines and copper compounds[164]. The formation of a new copper complex of the amine is responsible in this instant for the inhibiting effect[165]. The mechanism of the action of the synergistic mixture of an amine (AmH) with copper salts includes, together with the reactions known for each component, new stages[165] involving the complexes:

$$AmH + Cu(II) \rightleftarrows Cu(II)\cdot Am\dot{H}\,,$$

$$Cu(II)\cdot AmH + R\dot{O}_2 \rightarrow Cu(II)\cdot Am^{\cdot} + ROOH\,, \qquad (85)$$

$$Cu(II)\cdot Am^{\cdot} + R\dot{O}_2 \rightarrow Cu(II) + \text{product}, \qquad (86)$$

$$Cu(II)\cdot AmH + ROOH \rightarrow Cu(II)\cdot AmH + \text{product}. \qquad (87)$$

The mechanism describes quantitatively the characteristics of the initiated oxidation of ethylbenzene in the presence of a mixture of $CuSt_2$ and *p*-toluidine. An interesting feature of the action of such mixtures is the marked increase of their activity with increase of temperature[166]. The enhancement of the inhibition is caused by the formation of a new product of the thermal transformation of the primary complex, which has a higher inhibiting activity. It has been shown in recent years that the synergistic effect can be exhibited by mixtures of inhibitors reacting with the radicals $R\dot{O}_2$ (aromatic amines and phenols) and with acceptors of the radicals $\dot{R}$ (quinones and nitroxy-radicals),[167] as well as mixtures of u.v. absorbers and antioxidants[168]. As a consequence of the diffusion of the inhibitors from the bulk of the specimen to the surface layer, the synergistic effect greatly increases in the solid phase (diffusion synergism)[169].

9. Critical Phenomena in Liquid-Phase Oxidation

Analysis of kinetic equations for degenerate branched chain reactions with linear chain termination (for example, by an inhibitor) has demonstrated the possibility of the existence of limiting phenomena[170] of the kind observed in fully branched chain processes.

At a constant rate of initiation of the free radicals, the inhibitor is consumed linearly at a rate

$$-d[InH]/dt = w_i/f\,. \qquad (88)$$

In a degenerate branched chain reaction the inhibitor is consumed during the period of inhibition with self acceleration [in contrast to reaction (88)] as a consequence of the increase of the rate of initiation of chains during the reaction. For certain values and ratios of the rate constants for the elementary stages, there is a possibility of a progressive increase of the inhibition periods up to a sharp arrest of the reaction at a certain inhibitor concentration $[InH]_{cr}$.

For branched chain processes, the concentrations of the hydroperoxide and free radicals under the conditions of chain termination by the inhibitor are given by the equations

$$[R\dot{O}_2] = \frac{w_0 + \delta k_p [ROOH]}{f k_7 [InH]}\,, \qquad (89)$$

$$\frac{d[ROOH]}{dt} = \nu w_0 + \varphi [ROOH]\,, \qquad (90)$$

where $\nu = k_2[RH]/fk_7[InH]$ is the chain length, $w_i = w_0 + \delta k_p[ROOH]$ the rate of chain initiation, and $\phi = \delta k_p(\nu - 1/\delta)$ the reaction self-acceleration factor.

It follows from Eqn.(90) that, for $\phi > 0$, i.e. when $\nu > 1/\delta$, the hydroperoxide accumulates with self acceleration: $d[ROOH]/dt > 0$. For $\phi > 0$, i.e. when $\nu < 1/\delta$, conditions in which the hydroperoxide concentration may be assumed to be quasi-stationary, i.e. $d[ROOH]/dt = 0$, are established after a time interval. The change in conditions occurs at $\phi = 0$ ($\nu = 1/\delta$), which determines the critical inhibitor concentration:

$$[InH]_{cr} = \frac{\delta k_2 [RH]}{f k_7}\,. \qquad (91)$$

The limiting phenomena were first observed in the oxidation of n-decane catalysed by copper stearate[107].

The characteristic features of the critical phenomena for metal complexes can be seen in relation to the kinetics of the oxidation of n-decane in the presence of bis{3-hydroxo-2-benzo[*b*]thenylideneanilinato}copper (CuL_2) (Fig.19). At low concentrations the copper chelate greatly accelerates the reaction. At high concentrations inhibition periods appear and increase sharply at a critical concentration $[CuL_2]_{cr}$.[172]

However, at the end of the inhibition periods the process takes place under catalytic conditions, owing to the consumption of the chelate down to low concentrations[172]. Since the rate constants for chain termination by metal complex inhibitors depend on the structure of the chelate unit, the critical inhibitor concentration depends on the nature of the chelate [according to Eqn.(91)].

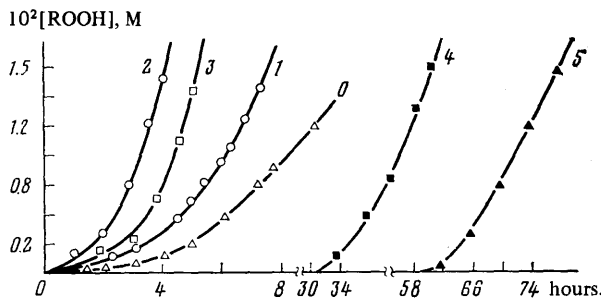


Figure 19. Kinetic curves for the accumulation of hydroperoxides in the oxidation of n-decane (120 °C) without a catalyst (0) and in the presence of bis{3-hydroxy-2-benzo[*b*]-thenylideneanilinato}copper(II) at different concentrations (M): 1) 1.5×10^{-6}; 2) 9.0×10^{-5}; 3) 1.1×10^{-4}; 4) 1.2×10^{-4}; 5) 1.5×10^{-4}.[171]

The existence of critical concentrations of transition metals has been established for simple and complex compounds of manganese, cobalt, and other metals[170]. Critical phenomena are also observed for phenols and aromatic amines[1,173].

Limiting phenomena occur in the oxidation of n-butane under pressure when the hydrocarbon is diluted with benzene. The reaction proceeds at a high rate only when the mole fraction of butane is ≥0.28, the process undergoing a sharp arrest when butane is consumed to give this dilution[174]. By taking into account the limiting phenomena, it is possible to explain the arrest of the oxidation of n-decane in the presence of potassium permanganate[175].

Limiting phenomena should be observed for a fairly high rate constant for the decomposition of hydroperoxides into free radicals and a low chain initiation rate constant[171]. In this case there are short inhibition periods τ in the region of inhibitor concentrations below the critical value and there is a sharp increase of τ following the attainment of limiting conditions where the rate of the process is determined mainly by the rate of chain initiation. The critical phenomena for organic inhibitors and metal complexes are therefore observed in most cases when the hydroperoxides decompose with participation of metal-containing catalysts.

Distinct limiting phenomena are observed in the continuous inhibited oxidation of hydrocarbons (open systems).[176] The critical inhibitor concentration is in this case given by[177]

$$[\mathrm{InH}]_{cr} = i_{cr} = \left(\sqrt{i_{\varphi=0}} + \sqrt{w_0/fv}\right)^2,$$

where $i_{\phi=0}$ is the inhibitor concentration defined by Eqn.(91) and w_0 is the rate of chain initiation.

Fig. 20 illustrates the accumulation of hydroperoxides in the oxidation of n-decane under conditions where the hydrocarbon with different concentrations of α-naphthol is continuously supplied into the reaction vessel and the oxidised product is removed from it, also continuously, at the same rate. Evidently a sharp change in the process conditions occurs for a slight alteration of the InH concentration in the entering solution—from 9.0×10^{-6} to 9.05×10^{-6} M.[176]

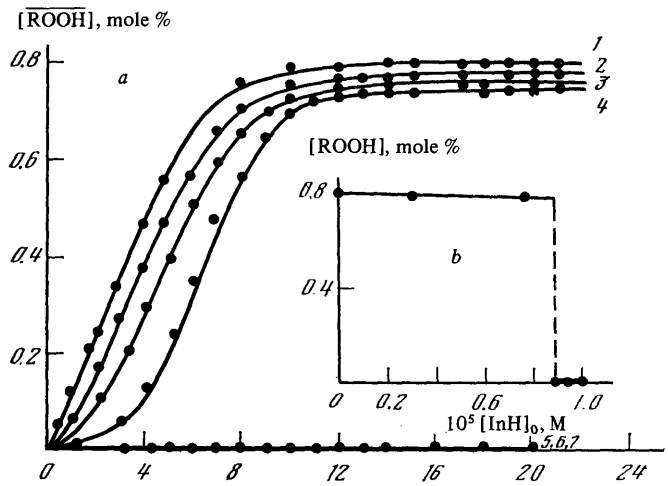


Figure 20. *a*) Kinetic curves for the accumulation of the hydroperoxide in the oxidation of n-decane in an open system in the presence of α-naphthol. Inhibitor concentration in the solution entering the vessel (M): 1) 0.0; 2) 3×10^{-6}; 3) 7.5×10^{-6}; 4) 9.0×10^{-6}; 5) 9.05×10^{-6}; 6) 1.2×10^{-5}; 7) 1.4×10^{-5}; *b*) dependence of the stationary concentration of the hydroperoxide on the inhibitor concentration[176].

III. KINETICS OF THE AGEING OF POLYMERS AND THEIR STABILISATION

Much attention has been devoted to the chemical kinetics of the ageing of polymers and to problems of their stabilisation as one of the branches of the modern science of macromolecular compounds. The knowledge of the kinetics and principal parameters of ageing makes it possible to predict the useful life and the optimum utilisation of polymeric materials. The results of kinetic studies of the ageing of polymers also make it possible to put forward the fundamental principles of the selection of effective stabilisers, increasing the quality of polymeric materials and their useful life.

During two decades, this field has greatly developed. It has become a special branch of the chemistry of the solid state in which studies are made of complex coupled radical-chain, ionic, and molecular reactions under the conditions of solid polymeric matrices with participation in the chemical process of the polymeric molecules of the matrix[178,179].

Specific types of the ageing of polymeric materials—thermal and thermo-oxidative ageing, ageing under the influence of light, penetrating radiation, and mechanical degradation, ageing under the influence of corrosive chemicals, biochemical and microbiological ageing, etc.—have been examined in a large number of monographs[180–190]. The experimental results obtained in recent years at the Institute of Chemical Physics of the USSR Academy of Sciences have been published recently[178,179]. In the present section we shall therefore briefly summarise the principal ideas of the chemical

physics of the ageing of polymers and the principles and problems of the stabilisation of polymers and polymeric materials.

1. The Ageing of Polymers as a Multifactorial Problem

The ageing of polymers can be defined as a set of chemical and physical transformations occurring in the polymer during its use, processing, or storage and leading to its losing a set of useful properties. Here one must bear in mind that the polymer is acted upon by numerous factors: heat, light, penetrating radiation, oxygen moisture, corrosive chemical compounds, and mechanical loads; therefore the ageing of the polymers must be considered as a multifactorial problem.

From the point of view, a system of equations for a multidimensional space can be proposed for the description of the time variation of the properties Y_i of a polymeric material under conditions X_i:[178]

$$Y=f(X, t)\ . \qquad (92)$$

The material is suitable for use in the course of a certain period τ, after which, under conditions X, the point Y leaves the region of operational suitability ε_0 in this space (Fig. 21). The solution of Eqns. (92) would make it possible to determine the useful life of the polymer τ. In principle, this problem is susceptible to solution in a general form by modern computer techniques. The following processes are usually considered: thermal degradation, photodegradation, mechanodegradation, oxidation, hydrolytic degradation, etc.—these are limiting cases of the ageing process in which the changes in the properties of the material are determined by one factor only.

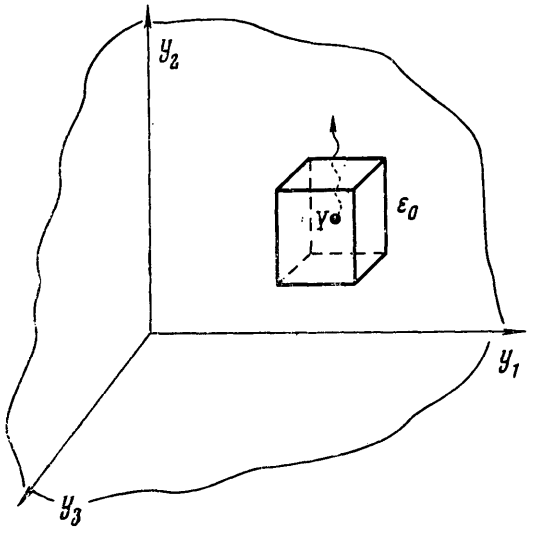


Figure 21. A qualitative picture of the time variation of the set of properties of a polymer Y (special case—point in a three-dimensional space); ε_0—the region of the operational suitability of the polymer[178].

In the general case ageing involves three stages: initiation—the stage in which active ageing centres are formed; development of ageing—the principal stage determining the changes in the properties of the polymeric material; the stage in which the active ageing centres are destroyed.

The physicochemical nature of the initiation of ageing can be various. For example, in photoageing this involves the formation of free radicals or ions under the influence of light, the appearance of ions, electrons, and radicals under the influence of radiation, and in mechanodegradation the initiation consists in the dissociation of molecules by mechanical forces with formation of free radicals.

External factors determine in the first place the initiation stage. Certain influences act also on the development of ageing. For example, the presence of oxygen converts the entire process into an oxidative reaction (thermal degradation becomes thermal oxidation, photolysis becomes photooxidation, and mechanodegradation becomes oxidation in the field of mechanical forces). Temperature influences all the elementary stages with the exception of processes whose activation energy is close to zero.

2. The Nature of the Active Centres

One of the principal problems of the chemical physics of ageing and the stabilisation of polymeric materials is the determination of the nature of the active centres responsible for the ageing of polymers and the mechanisms of their migration. It can now be regarded as to a large extent solved: the principal types and chemical nature of the active centres and their electronic structure have been determined, methods have been developed for the identification and measurement of the number of active centres, and the principal reactions and in many instances also their quantitative characteristics (rate constants on activation energies) are known[191,192].

The chemical reactions in the ageing of polymers proceed in most instances with participation of three types of active species: free radicals, excited species, and, to a lesser extent, ions. It has been shown in many studies that free radicals play the main role in the ageing of polymeric materials, which is due to the fact that reactions involving either the homolytic dissociation of the main molecular chain or the homolytic abstraction of atoms or radicals from side groups are characteristic of the majority of polymers. The structure and properties of the free radicals participating in the ageing of polymers and polymeric materials have been thoroughly investigated by EPR.[193] The central and terminal macroradicals and polymer radical-ions have been identified, the formation of low-molecular-weight radicals in the decomposition of macroradicals and the formation of radicals from stabiliser molecules have been demonstrated, and the formation of radical pairs has been observed.

Ions are formed in polymers usually only at the stage involving the initiation of the radiation processes associated with the degradation of polymers in corrosive media. Unfortunately, owing to the lack of special methods resembling EPR, it is much more difficult to identify the active centres in degradation by an ionic mechanism. In this field there have been virtually no systematic studies, with the exception of those concerning the degradation of certain natural polymers in solution[189].

Electronically excited molecules in the lowest excited singlet or lowest triplet states can play the most important role in the photochemical ageing of polymers. Two-quantum photochemical processes with participation of the highest triplet states as well as certain labile species in an excited state, for example, "hot" free radicals, are important[186,187].

3. Kinetics of the Polymer Ageing Processes

The thermal oxidation and photo-oxidation of polymers have been most thoroughly investigated, apparently because these processes are very close to the liquid-phase oxidation reactions of organic substances, which have been thoroughly studied.

The rate constants for the elementary reactions in polymers have been usually measured by modifications of methods developed previously for liquid-phase processes[178]. The rate of initiation w_i has been measured by the method of inhibitors in various versions and also by determining the induction period of the inhibited oxidation. The chain termination rate constant has been determined from the equation $k_t = w_i/[R\dot{O}_2]^2_{st}$, if the stationary concentration of peroxy-radicals is known, or by a non-stationary method based on the kinetics of the destruction of the radicals $R\dot{O}_2$ formed in the polymer, for example, after brief exposure to ultraviolet light. The parameter $k_p/k_t^{1/2}$, characterising the susceptibility of the polymer to oxidation, has been determined from the rates of the initiated chain oxidation (w_i = const.).

The kinetic parameters obtained showed that, compared with the liquid phase, the absolute values of the rate constants for the elementary processes in the solid polymer are usually smaller and the activation energies are higher. In addition, the differences between the relative reactivities of substances of different chemical types involved in isotypical chemical processes diminish ("level off"), which is due to the difficulty of the transport of reactants and the stability of the walls of the cage surrounding the reaction centres, which are characteristic of the solid phase[178].

The kinetics of the thermo-oxidative and photo-oxidative ageing processes for polymers in a highly elastic state and many semicrystalline polymers above their glass points qualitatively differ little from the kinetics of the oxidation of melts and low-molecular-weight organic substances. As an example, one may quote the oxidation of a polypropylene powder at low temperatures using a highly sensitive manometric apparatus which permits the measurement of the amount of absorbed oxygen from the very earliest oxidation stages (Fig. 22).[194]

The oxidation of films of isotactic polypropylene at 130 °C, investigated up to more advanced reaction stages, proceeds similarly (Fig. 22b). The process takes place with self-acceleration: its rate increases from the very beginning and at a degree of oxidation of ~15% reaches a maximum, after which it gradually falls. The variation of the rate of oxidation parallels the accumulation of hydroperoxides (Fig. 22b, curve 3), which indicates the decisive role of hydroperoxides in the propagation of polymer oxidation processes[195].

Thus the oxidative ageing of polymers is a degenerate branched chain reaction. It has been shown at a quantitative level that the photo-oxidation of polyolefins (PH) is described by the following kinetic scheme[196]:

$$PH \rightarrow P\dot{O}_2,$$

$$P\dot{O}_2 + PH \xrightarrow{O_2,\, k_p} POOH + P\dot{O}_2 \text{ (propagation)},$$

$$POOH \xrightarrow{h\nu} P\dot{O} + \dot{O}H \rightarrow 2P\dot{O}_2 + S \text{ (branching)},$$

$$[C{=}O] \xrightarrow{h\nu} P\dot{O}_2 + S,$$

$$P\dot{O}_2 + P\dot{O}_2 \xrightarrow{k_t} [C{=}O] \text{ (termination)},$$

where [C=O] are carbonyl compounds and S represents the step involving the dissociation of macromolecules. The rate constants for all the elementary reactions in the above scheme, which are required for the description of the kinetics of the accumulation of products, were determined by independent methods. The agreement between calculations and experiment confirmed the reliability of the proposed scheme.

In the course of their ageing, processes characteristic only of high-molecular-weight compounds take place in the polymers: degradation and cross-linking, the formation of cross-linked three-dimensional structures, and the propagation of reactions along the polymer chain.

The specific features of the structure of macromolecules are manifested, for example, in the kinetics of thermal degradation. The presence of two macroscopic thermal degradation stages is characteristic of the majority of polymers[197]. In the initial stage the process proceeds at a relatively high rate and with a low activation energy. At advanced stages the

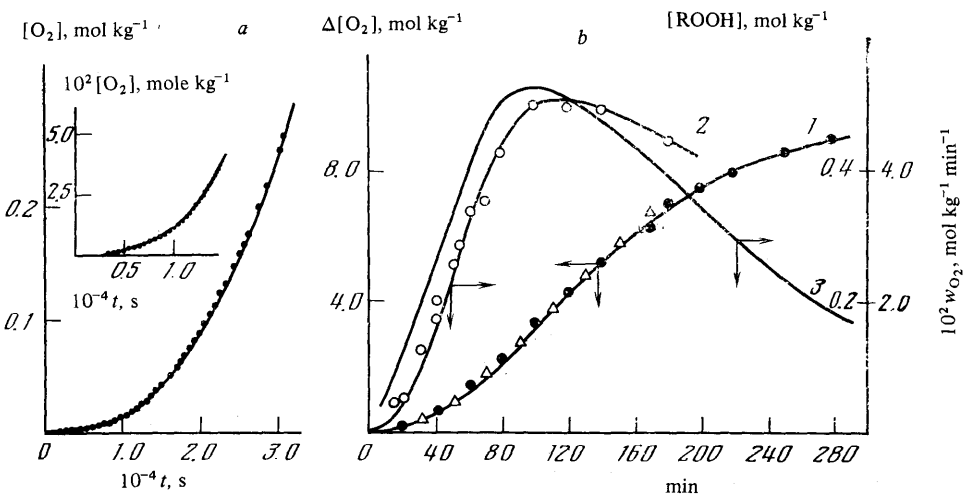


Figure 22. a) Kinetic curves for the absorption of oxygen in the autoxidation of polypropylene powder at 92 °C (the inset shows the initial stages of the process)[194]; b) kinetic curves for the autoxidation of polypropylene films at 130 °C: 1) absorption of O_2; 2) variation of the rate of oxidation; 3) accumulation of hydroperoxides[195].

rate of degradation falls and the activation energy increases. The fraction of the substance decomposing in the first stage depends on the method of synthesis of the polymer (Fig. 23).

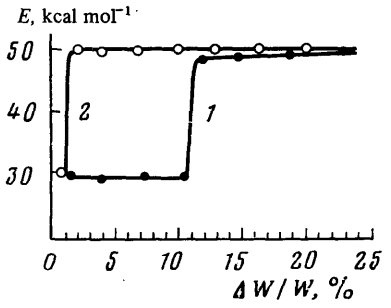


Figure 23. Dependence of the activation energy for the thermal degradation of polyvinyltoluene obtained by radical (curve *1*) and anionic (curve *2*) polymerisation on the degree of conversion (weight loss) $\Delta W/W$.[197]

The low activation energy for the initial stage is evidently associated with the fact that at this stage weak bonds or defective sites in macromolecules are ruptured. Only after they have been used up does the degradation of the normal strong bonds in the polymer begin. The artificial creation of defects in the polymer by its photolysis or preliminary oxidation can lead to the complete disappearance of the second, slower stage of the process. On the other hand, the formation of a defect-free structure makes the concentration of weak bonds insignificant, which has been achieved in polycaproamide.

4. Characteristics of the Chemical Reaction in the Polymer Matrix

The non-equivalence of the local properties of the environment of the reactive centres and correspondingly their spatially different chemical reactivities are characteristics of polymers as structurally inhomogeneous systems. Chemical reactions therefore occur in the first place in those regions where the conditions are most favourable. As a result, at a certain degree of conversion, the reactions are strongly retarded—the so-called "kinetic arrest of the reaction" is observed. A change of conditions, for example of temperature, leads to the renewal of the reaction. As an example, Fig. 24 illustrates the kinetics of the destruction of macroradicals in polymethacrylic acid under the conditions of a stepwise variation of temperature. The phenomenon of the "kinetic arrest" of the reaction has been observed in a wide variety of processes in solid polymers[178]. Methods have now been developed for the description of processes of this kind with the aid of the so-called polychromatic kinetics[198,199,200]. The variation of the macroscopic concentrations of the reactants is described by an integro-differential equation, which assumes the following form in the case of the simplest unimolecular reaction:

$$\frac{d[A]}{dt} = -\int_0^\infty kA(k)\,dk\,, \qquad (93)$$

where $A(k)$ is the density of the distribution of the concentration of substance A with respect to its reactivity, characterised by the chemical reaction rate constant k. The distribution $A(k)$ varies with time both due to the chemical transformation of substance A, described by Eqn. (93), and due to relaxation and diffusion processes, which alter the local properties of the medium around the reaction centre.

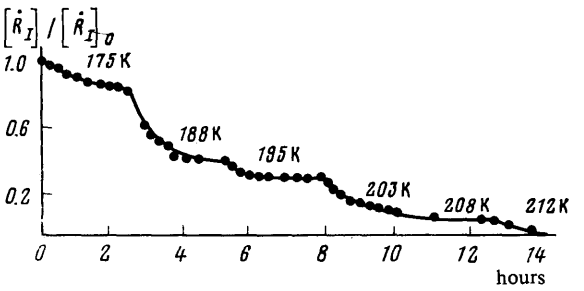


Figure 24. Kinetic curves for the thermal decomposition of central macroradicals in polymethacrylic acid in the temperature range 175–212 K.[221]

At temperatures considerably below the glass point of the polymer the process proceeds, as it were, in microreactors with unaltered local properties. Solution (93) then has the form of an integral Fredholm equation of the first kind:

$$[A] = \int_0^\infty e^{-kt}A(k)\,dk\,. \qquad (94)$$

Thus the kinetic curve for the variation of the concentration of A is a representation (in the sense of a Laplace transformation) of the initial distribution function $A(k)$. The form of the function $A(k)$ can be obtained from the kinetic curve $[A](t)$ by the reverse Laplace transformation.

The principles of polychromatic kinetics made it possible to calculate the distributions of species with respect to rate constants, activation energy, and activation entropy and to establish the fundamental mechanisms of the averaging out of the kinetic non-equivalence of the species and the conditions for the transition from polychromatic to monochromatic kinetics[191].

The kinetics and direction of chemical reactions in solid polymers are influenced significantly by the molecular dynamics and physical structure of the polymer, which occurs as a consequence of a change in the translational diffusion coefficients of the low-molecular-weight reactants or a change in the frequencies and amplitues of the segmental movements of the macromolecules and macroradicals, which influence directly the chemical reaction step itself.

It is well known that mobility influences the kinetics of the destruction of macroradicals in solid polymers—the rate of destruction decreases on transition from the amorphous to the crystalline phase, the rate constant for the destruction in oriented specimens is lower than in non-oriented specimens, the stability of macroradicals increases when the polymer is cross-linked, the rate of destruction of macroradicals in three-dimensional polymers increases with increase in the length of the oligomeric block, etc.

The molecular mobility has been varied[201,202] by altering the external pressure and by introducing into the polymer chemically inert solvents, which induced plasticisation. Under

these conditions, the rate constants for the recombination of radicals in amorphous polymers decreased with increase of pressure at temperatures above T_g. The destruction of peroxy-radicals in polystyrene[203] and polypropylene[204] was accelerated by the addition of small amounts of benzene.

The influence of molecular mobility on the rates of reaction of phenoxy-radicals with polyolefin hydroperoxides[205,206] and of nitroxy-radicals with phenols[207] in solid polyolefins has also been studied. It was found that the rates of these reactions are independent of the nature of the polymer and increase following the addition of aromatic solvents, whose role reduces to increasing molecular mobility. The increase of the rate constants for the above reactions is correlated with the increase of the frequency of rotation of the paramagnetic probe[205,207].

In mechanodegradation the change in the lifetime of the polymers cannot be described by taking into account only the changes in the rate constant for the elementary chemical processes in accordance with the Zhurkov equation

$$k = k_0 e^{-\frac{E-\gamma\sigma}{RT}}, \qquad (95)$$

where E is the activation energy, σ the mechanical stress, and γ a proportionality coefficient. A radical chain mechanism agrees only qualitatively with the experimental results. It has been shown[208,209] (Fig. 25) that mechanical stresses do not exert an appreciable influence on the rate of formation of radicals in chemical or radiation-chemical initiation and hence on the rate of degradation of macromolecules initiated by these radicals. At the same time the lifetime of polymers

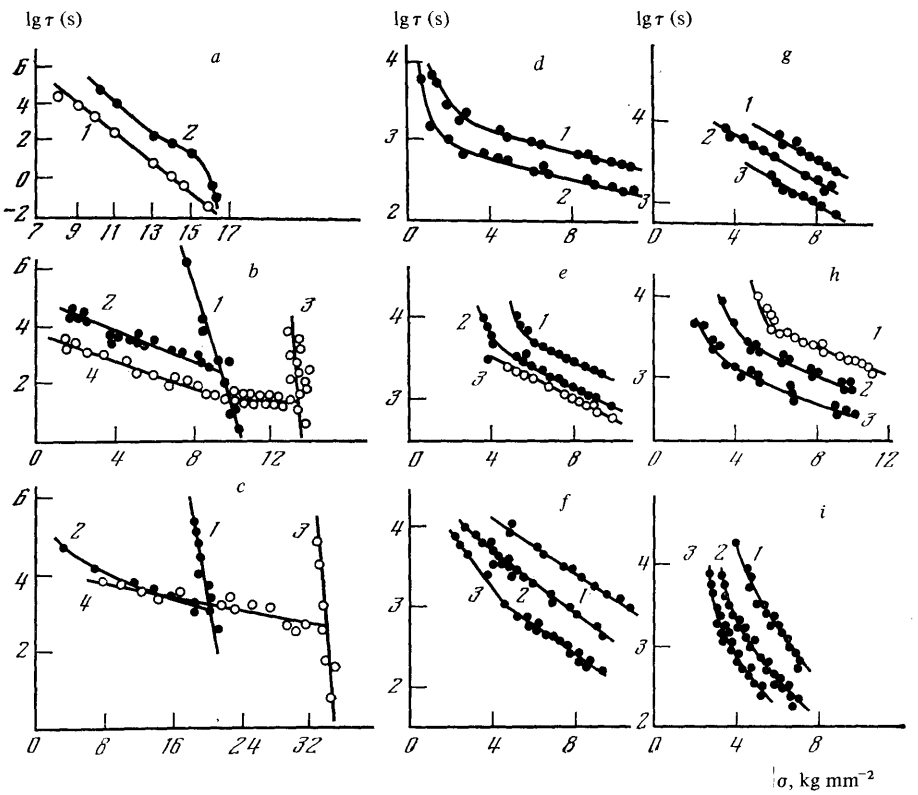


Figure 25. Variation of the lifespan of the polymer (τ) under a mechanical stress (σ) due to the introduction of an inhibitor (*a*) [222] and initiators (*b*–*i*) [209] of radical reactions: *a*: 1) pure nitrocellulose; 2) nitrocellulose with added 0.3% of the 4-ethyl-4-hydroxy-2,2,6,6-tetramethylpiperdin-1-yloxy-radical; *b*) 1,2-polycarbonate and 3,4[sic]-triacetylcellulose containing added $FeCl_3$, without (curves *1* and *3*) and with (curve *2*) photolysis of the additive; *c*) 1,2-poly(ethylene terephthalate) and 3,4-polycaproamide containing added $FeCl_3$, without (curves *1* and *2*) and with (curve *3*) photolysis of the additive; *d*) photodecomposition of triacetylcellulose without additives [1) 314 K; 2) 360 K; unfiltered light of DRSh-500 lamp; $I = 1.6 \times 10^{21}$ m^{-2} s^{-1}]; *e*) photodecomposition of triacetylcellulose with 0.6 wt.% of naphthalene [1) 286 K; 2) 301 K; 3) 323 K; nitrogen; $I = 2.6 \times 10^{21}$ m^{-2} s^{-1}; $\lambda > 300$ nm]; *f*) photodecomposition of triacetylcellulose with 9.1 wt.% of benzoyl peroxide [1) 303 K; 2) 325 K; 3) 348 K; air; $I = 0.4 \times 10^{21}$ m^{-2} s^{-1}; $\lambda > 300$ nm]; *g*) photodecomposition of triacetylcellulose with 0.16 wt.% of $HFeCl_4$ [1) 293 K, air depleted in oxygen; 2) 293 K; 3) 308 K; air; $I = 0.6 \times 10^{20}$ m^{-2} s^{-1}; $\lambda > 340$ nm]; *h*) photodecomposition of triacetylcellulose with 1.1 wt.% of naphthalene [1) 304 K; 2) 329 K; 3) 360 K; air; $I = 1.6 \times 10^{21}$ m^{-2} s^{-1}; $\lambda > 300$ nm]; *i*) thermal decomposition of triacetylcellulose with 9.1 wt.% of benzoyl peroxide [1) 378 K; 2) 388 K; 3) 393 K; air].

diminishes with increasing stress, i.e. a smaller number of breaks in macromolecules becomes sufficient for their decomposition. The breakdown of the specimen is not therefore related to the occurrence of a critical number of breaks, as suggested previously. The decomposition of the polymer is determined not only by the kinetics of its chemical degradation but also by the kinetics of the physical relaxation processes as a result of which the structure of the polymer changes after the breaks in the molecules.

5. Relation Between Practically Important Properties of the Polymers and the Kinetics of Ageing

Knowledge of the kinetics of the changes in their physicomechanical characteristics, for example, the relative elongation on rupture, the ultimate tensile strength, etc., is important in the practical utilisation of polymeric materials. The determination of the detailed ageing mechanism made it possible to relate the changes in these properties under various operating conditions for the polymers to the kinetic characteristics of their ageing. In particular, this relation has been established for the photo-oxidation of polypropylene[210].

Fig. 26 presents kinetic curves for the variation of the relative elongation in the photo-oxidation of various specimens of polypropylene (PP) under the influence of light of different intensity and spectral composition. Despite the fact that the curves have different shapes, they can be made to coincide when the number of breaks in the macromolecular chain Ω during the process time is plotted along the abscissa axis.

The number of breaks is defined as the sum of steps involving the photodecomposition of branching products—hydroperoxides and carbonyl compounds:

$$\Omega = \int_0^t (\alpha [\text{ПООН}] + \alpha' [\text{C=O}])\, dt \ . \qquad (96)$$

Thus the dynamics of the variation of the physicomechanical properties of the polymer is related to the kinetics of the chemical ageing process and calculations can be made on the latter using measurements of its kinetic characteristics.

6. Fundamental Principles of the Stabilisation of Polymeric Materials

The known methods of stabilising polymeric materials can be classified in terms of the stage of the ageing process on which they act. A large group of stabilisers comprises substances which decrease the probability of the formation of active centres at the initiation stage. They include agents quenching excited states ("quenchers")—substances which react with admixtures catalysing the decomposition of polymers. Stabilisers which deactivate chemically active reaction products, for example, substances which decompose hydroperoxides, are particularly important.

The stabiliser influencing the propagation stage of the ageing process, for example, the oxidation chain propagation stage, include substances which prevent the penetration of oxygen into the polymeric material or lower its concentration in the material.

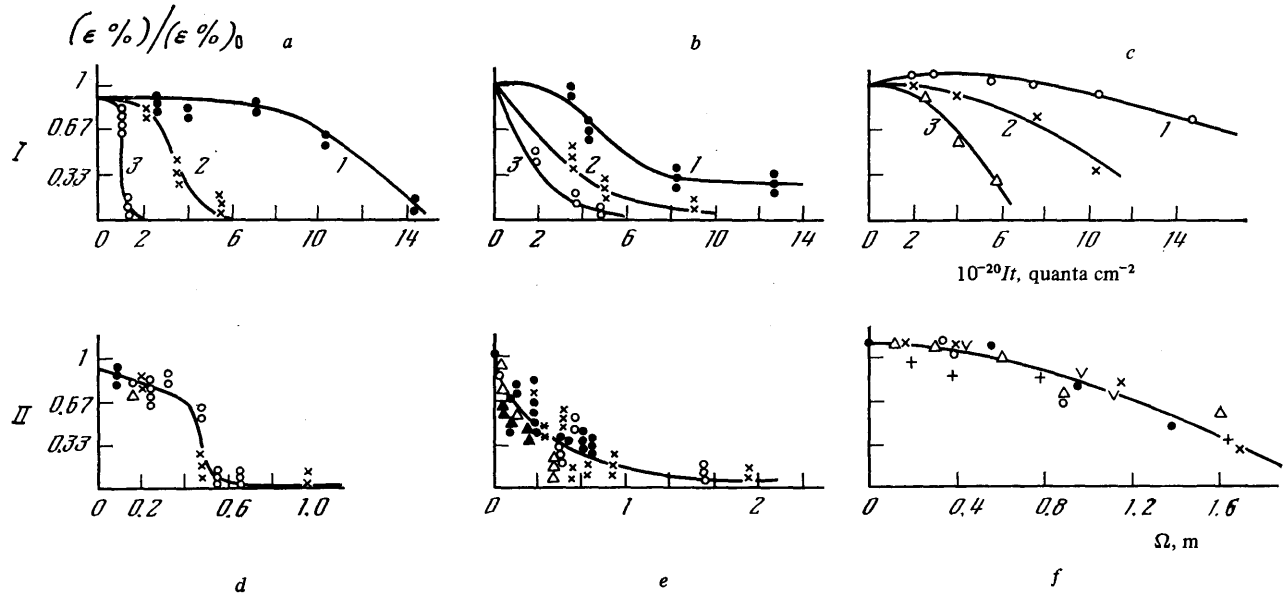


Figure 26. Variation of the relative elongation on rupture in the course of the photo-oxidation of polypropylene: *a*)–*c*) dependence on the amount of light with λ = 254 nm incident on the specimen [light intensity (10^{-15} *I*, quanta cm^{-2} s^{-1}): 1) 4; 2) 0.7; 3) 0.24]; *d*)–*f*) dependence on the number of breaks in the macromolecules of the specimen in a given time; *a*) and *d*) isotropic specimen; *b*) and *e*) oriented annealed specimen; *c*) and *f*) oriented specimen (950%).[178]

The class of stabilisers accelerating the stage involving the destruction of active centres, for example, the acceptors of free radicals or the inhibitors of free radical processes InH, is most widely used in practice and has been most thoroughly investigated. The mechanism of the action of such substances and the criteria used to estimate their efficiency were examined in detail above (Section II, 7). As in the liquid-phase oxidation of hydrocarbons, critical inhibitor concentrations have been observed in the oxidation of polymers, above which the inhibition period of the oxidative degradation increases sharply. A synergistic effect, arising when various stabilising compositions are used, has also been observed[211-213].

The kinetic characteristics are usually determined at comparatively low stabiliser concentrations. The region of extensive inhibition of autoxidation at sufficiently high concentrations (much higher than the critical concentration), usually employed under technological conditions, is of practical interest. Kinetic analysis is significantly simplified under these conditions by the fact that the quasi-stationary principle becomes applicable not only to free radicals but also to the branching product—the hydroperoxide. For example, the mechanism of the inhibited oxidation by sterically hindered phenols can be described as follows[214]:

$$\text{initiation} \xrightarrow{+O_2,\ w_0} R\dot{O}_2\ ,$$
$$R\dot{O}_2 + RH \xrightarrow{+O_2;\ k_2} ROOH + \dot{R}\ ,$$
$$ROOH \xrightarrow{+O_2;\ k_3} 2f R\dot{O}_2 + \text{product},$$
$$R\dot{O}_2 + PhOH \xrightarrow{k_7} ROOH + Ph\dot{O}\ ,$$
$$R\dot{O}_2 + Ph\dot{O} \xrightarrow{k_8} QP\ (\text{quinolide peroxides}),$$
$$Ph\dot{O} + Ph\dot{O} \xrightarrow{k_9} PhOH + \text{products},$$
$$QP \xrightarrow{+O_2,\ k_{11}} 2\delta R\dot{O}_2 + \text{products}.$$

In the presence of the effective antioxidant used in practice, the contribution of the remaining reactions is usually small.

Table 9 presents analytical expressions for the induction period τ, the critical concentration $[PhOH]_{cr}$, and the rate of consumption w_{PhOH} of the inhibitors—phenols of two types: (I) k_9 is small and the radicals $Ph\dot{O}$ are destroyed only via reaction (8); (II) k_9 is large and the radicals $Ph\dot{O}$ are destroyed only via reaction (9). Evidently the characteristics of the antioxidant activity (τ and w_{PhOH}) under the conditions used depend little on the antiradical activity of the inhibitors (on the constant k_7) and are largely determined by the constant for the interaction of the inhibitor radicals k_9 and the probability of the emergence of radicals from the cage in the decomposition of hydroperoxides (f) and quinolide peroxides (δ). In solid polymers f and δ are relatively low, which is consistent with the high antioxidant activity of the inhibitor. On passing to a melt, the antioxidant activity diminishes owing to the increase of f and δ, which is sometimes formally interpreted as a result of the additional formation of free radicals by inhibitor molecules.

In practice it is important to obtain from standard tests on stabilisers information necessary for predicting their effectiveness under the operating conditions. As mentioned above, on passing from the liquid phase to a solid polymer, the reactivity of stabilisers levels off. The relative reactivities of the species in the solid polymer (k_S) and in the liquid phase (k_L) are linked by the relation[215]

$$\frac{(k_1)_S}{(k_2)_S} = \left[\frac{(k_1)_L}{(k_2)_L}\right]^{1/2}. \qquad (97)$$

Eqn.(97) makes it possible to select stabilisers for polymeric materials (antioxidants, quenchers) on the basis of much less laborious experiments, carried out in model liquid-phase systems.

The influence of molecular physics on the chemical reactions in polymers leads to the discovery of new physical principles of the stabilisation of polymeric materials by specific structural-physical modification of the material (deformation, stress, orientation, isotropic compression, regulation of the supermolecular structure and morphology, etc.). For example, the rate of formation of the branching product (the hydroperoxide) diminishes in oriented polyolefins, which leads to an increase of the thermal stability of the oriented filaments compared with isotropic films[216]. There are many factors governing the stabilisation and the increase of the strength and lifetime of polymeric materials as a result of their structural-physical modification[191].

Table 9. Characteristics of the antioxidant activity of stabilisers under the conditions of extensive inhibition of oxidation[214]*.

Parameter	Type of phenol	
	I	II
$[PhOH]_{cr}$	$\frac{fk_2[RH]}{(1-f-\delta)k_7}$	$\frac{2fk_2[RH]}{(1-2f)k_7}$
τ	$\frac{2(1-f-\delta)(\gamma-1)^2[PhOH]}{\gamma^2 w_0}$	$\frac{2(1-2f)(\gamma-1)^2[PhOH]}{\gamma^{*2} w_0}$
w_{PhOH}	$\frac{w_0}{2(1-bf-\delta)}$	$\frac{w_0}{2(1-2bf)}$

*Here $b = 1 + \frac{k_2[RH]}{k_7[PhOH]}$; $\gamma = [PhOH]/[PhOH]_{cr}$.

7. Special Procedures for the Stabilisation of Polymers

Many stabilisers cannot be used at sufficiently high concentrations for a variety of reasons. In particular, some of them impart an undesirable colour to the polymeric material. Thermal stabilisers can be effective photosensitisers. The free radicals formed from stabiliser molecules in some cases enter into reactions promoting the decomposition of the polymer. Furthermore, the stabiliser can be consumed in useless side processes.

It is therefore desirable to produce stabilising compositions in such a way that the effective inhibitor acts in accordance with the *in statu nascendi* principle, i.e. in such a way that its main bulk is in a bound state, in a kind of "depot", and the active form of the stabiliser is released by it gradually or when necessary.

A quantitative criterion of the efficiency of the action of the inhibitor is *in statu nascendi* can be formed by analysing a simplified kinetic mechanism of the action of such an inhibitor on an initiated chain process.

$\xrightarrow{w_i} \dot{r}$—initiation of the formation of the active radical;

$Z \xrightarrow{k} \dot{R}$—the formation from the "depot" of the active form of the inhibitor $\dot{R}$, which behaves as a stabiliser (for simplicity, the stabiliser in a radical form is considered);

$\dot{R} + \dot{r} \xrightarrow{k_7}$—inhibition reaction;

$\dot{R} \xrightarrow{k_{10}} \dot{r}$—the generation of the active centre by a reaction involving the inhibitor.

The effectiveness of the stabilisation is characterised by the ratio of the rate of initiation to the rate of consumption of the active form of the inhibitor (for $k_{10} \gg k$):

$$\Psi = \frac{w_i}{\mathrm{d}[\dot{R}]/\mathrm{d}t} \cong \frac{w_i}{k[Z]} . \quad (98)$$

If the inhibitor is introduced into the system at the initial instant at a concentration $[Z]_0$, the efficiency of its action is determined by the expression

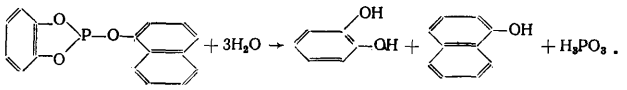
$$\Psi_0 = \frac{w_i}{w_i + 2k_{10}[Z]_0} . \quad (99)$$

Since $k_{10} \gg k$ by hypothesis, it follows that $\Psi > \Psi_0$. The ratio $\Psi/\Psi_0 = Q$ can serve as a criterion of the efficiency of the action of the inhibitor *in statu nascendi*:

$$Q = \frac{\Psi}{\Psi_0} = \frac{w_i + 2k_{10}[Z]_0}{k[Z]_0} \simeq \frac{2k_{10}}{k} . \quad (100)$$

Sterically hindered piperidines protect polymers from the action of light by the "depot" mechanism[217]. The mechanism of the light stabilisation of polymers by sterically hindered piperidines is more complex than that considered above. The piperidines themselves are not stabilisers but are converted under the influence of radiation into a mixture of nitroxy-radicals and other compounds which act as inhibitors.

Phosphorus acid esters, whose hydrolysis gives rise to the corresponding phenols or catechols, also function as a "depot":[218]



Clathrate compounds, from which the stabiliser is liberated on thermal decomposition and photodecomposition, can apparently also act via the "depot" mechanism.

Not only compounds from which the stabiliser is synthesised in the course of ageing but also the diffusion of the stabiliser to the degradation zone from another, undecomposed part of the polymer can be used as a stabiliser "depot". The diffusion phenomenon has been recently observed in the study of the photo-oxidation of polybutadiene films[219,220]. In the presence of an ultraviolet absorber light does not penetrate into the bulk of the polymer specimen. Photo-oxidation takes place only in the surface layer, which results in the consumption of the antioxidant (A). A concentration gradient of A is produced and the antioxidant diffuses from the bulk of the polymer to the surface layer. Since the deep layers serve as a source of inhibitor, thick specimens are oxidised more slowly than thin ones. It has recently been shown that this phenomenon is the main cause of the synergism observed in the stabilisation of polymers by mixtures of u.v. absorbers (UVA) and antioxidants, which interact with free radicals[219] or decompose hydroperoxides[220].

In the diffusion mechanism the synergistic effect depends on the ratio of the rates of reaction (w_r) and diffusion (w_d). For $w_r \gg w_d$, there is insufficient time for the diffusion of antioxidants to affect the process and synergism is not observed. The maximum effect can be obtained for the opposite condition: $w_d \gg w_r$. Here the entire oxidant is consumed in the inhibition of the photo-oxidation process in the photoreaction zone and the oxidation induction period is $\tau = \tau_0(L/l)$, where τ_0 is the induction period for $w_r \gg w_d$ and l and L are the thicknesses of the photoreaction zone and of the polymer films respectively.

The ideas developed concerning the mechanism of the synergism have created a scientific basis for the selection of effective synergistic mixtures which protect polymers from light-induced ageing, taking into account the properties of the polymer and the stabilisers, as well as the operating conditions. Within the framework of the mechanism examined, the requirements for the thickness of the specimens and for conditions under which accelerated tests of the light stability of polymers stabilised by synergistic mixtures must be performed also become understandable.

IV. KINETICS OF THE BIOLOGICAL PROCESSES

The living organisn is regarded as the most complex system of coupled chemical reactions under the influence and with participation of a multiplicity of chemical and physical factors, which initiate, catalyse, inhibit, and regulate these processes. This is responsible for the possibility of employing in biological and medical research methods and ideas characteristic of chemistry, physics, and mathematics.

Kinetic studies in biology permit quantitative estimates of the rate of propagation of the most important biological processes and of the influence on the latter by various factors as well as the establishment of quantitative criteria for the estimation of the efficiency of such influences. The mathematical description of the kinetics then involves a series of parameters which can be used to model the processes investigated and to analyse them using modern computer techniques.

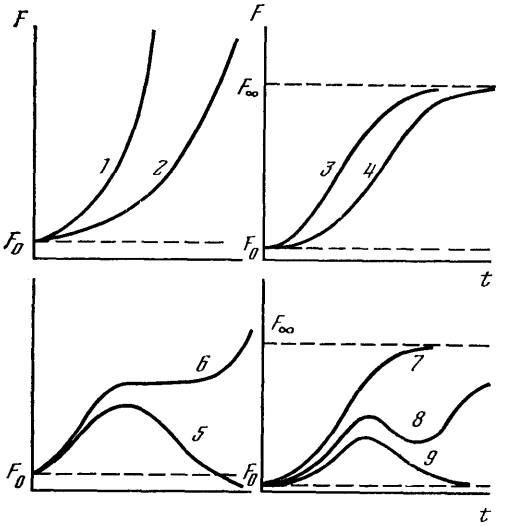


Figure 27. Plots of the functions used to described the kinetics of tumour growth. The analytical forms of the curves are presented in Table 10.[226]

Extensive kinetic studies on many pathological processes and phenomena—carcinogenesis, malignant growth, radiation damage, as well as the ageing of the living organisms—are being prosecuted at the present time[223–226]. The broad principles of the kinetic approach to the study of biological objects can be examined in relation to experimental tumour processes[226].

1. Kinetics of Tumour Growth

The differential equation for the growth of a tumour can be formulated as follows:

$$\frac{1}{F}\frac{dF}{dt} = \varphi(t) \quad , \qquad (101)$$

where $\phi(t) = \phi_1(t) - \phi_2(t)$ and F is the volume, diameter, or weight of the tumour, the number of tumour cells, or any other quantity characterising the growth of the tumour. The quantity $(1/F)(dF/dt)$ is the specific rate of growth, $\phi_1(t) \geq 0$ characterises the overall rate of multiplication of the cells, and $\phi_2(t) \geq 0$ characterises the overall rate of their destruction. The function $\phi(t)$ can be both positive and negative.

The overall form of the solution of the differential equation (101) is given by the expression

$$F = F_0 e^{\int \varphi(t)dt} \quad . \qquad (102)$$

Different deterministic models of the growth of a tumour can be reduced to the selection of the corresponding functions $\phi(t)$. Fig. 27 illustrates schematically the types of kinetic curves corresponding to the model functions frequently employed. Table 10 presents the corresponding kinetic equations. After the selection of the most suitable functions approximating the experimental data, regression analysis is carried out by standard methods. A linearising transformation is usually performed for the function F, which simplifies the calculation of the kinetic parameters.

Table 10. Functions used to describe the kinetics of tumour growth.

Name of function	Type of $\varphi(t)$	Differential equation*	No. of curve in Fig. 27
Exponential	$\varphi = \text{const}$	$F = F_0 e^{\varphi t}$	1
Exponential with a constant term	$\varphi = \frac{1}{1/a + c \cdot e^{-at}}$	$F = F_0 e^{at} + F_1$	—
Power	$\varphi = \frac{b}{t+a}$	$F = F_0 \left(1 + \frac{t}{a}\right)^b$	2
" "	$\varphi = \frac{b}{t+a} - c$	$F = F_0 \left(1 - \frac{t}{a}\right)^b e^{-ct}$	—
Gompertz function	$\varphi = ae^{-bt}$	$F = F_\infty \exp\left\{-\frac{a}{b} e^{-bt}\right\}$	3
Logistic function	$\varphi = \frac{b}{1 + e^{bt/a}}$	$F = \frac{F_\infty}{1 + ae^{-bt}}$	4
Bertalanphi function	$\varphi = \frac{be^{-bt}}{1/a - e^{-bt}}$	$F = F_\infty (1 - ae^{-bt})$	—
Polynomial function	$\varphi = \varphi_0 + \varphi_1 t + \cdots + \varphi_s t^s$	$F = F_0 \exp\left\{\varphi_0 t + \frac{1}{2}\varphi_1 t_2 + \cdots + \frac{1}{s+1}\varphi_s t^{s+1}\right\}$	5, 6
Asymmetric polynomial exponential function	$\varphi = (a_0 + a_1 t + \cdots + a_s t^s) e^{-bt}$	$F = a \exp\{[c_0 + c_1 t + \cdots + c_s t^s] e^{-bt}\}$	7, 8, 9

*Here a, b, and c are constants.

Extensive experimental data on the kinetics of the growth of tumours have now accumulated [226]. More than 60 experimental strains of solid and ascites transplantable and spontaneous animal tumours and leukaemias have been investigated. The equations presented above are used for a formal kinetic description of the development of these malignant processes.

An exponential relation is fairly frequently used both in experimental studies and for the analysis of the growth of human tumours. Fig. 28*A* presents generalised kinetic curves for exponentially growing animal tumours in terms of the dimensionless coordinates $\eta = e^{\theta}$, where $\eta = F/F_0$ and $\theta = \phi t$.

In principle, the most general type of kinetic curve is an S-shaped curve, because it is natural to expect that F tends to a limiting value in the course of the growth of the tumour by virtue of the characteristics of the development of tumours in the organism. In those cases where a logistic function of the type $F = F_\infty/(1 + ae^{-bt})$ is applicable to the description of the kinetics of the growth of such tumours, it is possible to construct a generalised plot in terms of the variables of the equation $\eta = 1/(1 + e^{\theta})$, where $\eta = F/F_\infty$ and $\theta = \ln a = bt$ (Fig. 28*B*).

For a comparative analysis of the rates of growth of different experimental tumours, one can use the maximum specific rate of growth ϕ_{max}. [226] For tumours growing exponentially, $\phi_{max} = \phi$.

Analysis of the distribution of 62 experimental tumours with respect to ϕ_{max} showed that the cumulan of the distribution in the range from $\phi_{max} = 0$ to 0.7 day^{-1} is linear, i.e. that the distribution of ϕ_{max} in this range is virtually uniform. From this it follows that tumours can apparently exist with arbitrarily small specific rates of growth. Approximately 80% of the tumours examined in terms of their values of ϕ_{max} fall within this linear range. There are many fewer tumours for which $\phi_{max} > 0.8$ day^{-1}.

2. Kinetic Criteria for the Estimation of the Effictiveness of Antitumour Preparations

The study of the kinetics of the development of tumour processes has made it possible to develop a series of criteria of the effectiveness of a particular therapeutic agent. For this purpose, it is necessary to compare control and experimental kinetic curves.

In the simplest case where tumour growth takes place exponentially both in the control,

$$F_c = F_0 e^{\varphi_c t} \qquad (103)$$

and in the experiment,

$$F_e = F_0 e^{\varphi_e t} \quad , \qquad (104)$$

the ratio

$$\varkappa = \varphi_e/\varphi_c \quad , \qquad (105)$$

showing by what factor the rate of development of the experimental process is reduced compared with the control, can be used as a measure of the effectiveness. For exponentially growing tumours, this criterion was introduced in 1962 [227] and was subsequently used in many investigations.

A series of criteria, used independently of the type of kinetic curves for the tumour growth in the control and in the experiment, have also been proposed [226]. In particular the criterion

$$\varkappa_9' = 1 - (\bar{F}_{te}/\bar{F}_{tc})\,100 \quad , \qquad (106)$$

which is called the percentage inhibition, is frequently used in the USSR. Here $\bar{F}_{te}$ is the average experimental value of F and $\bar{F}_{tc}$ is the value for the control.

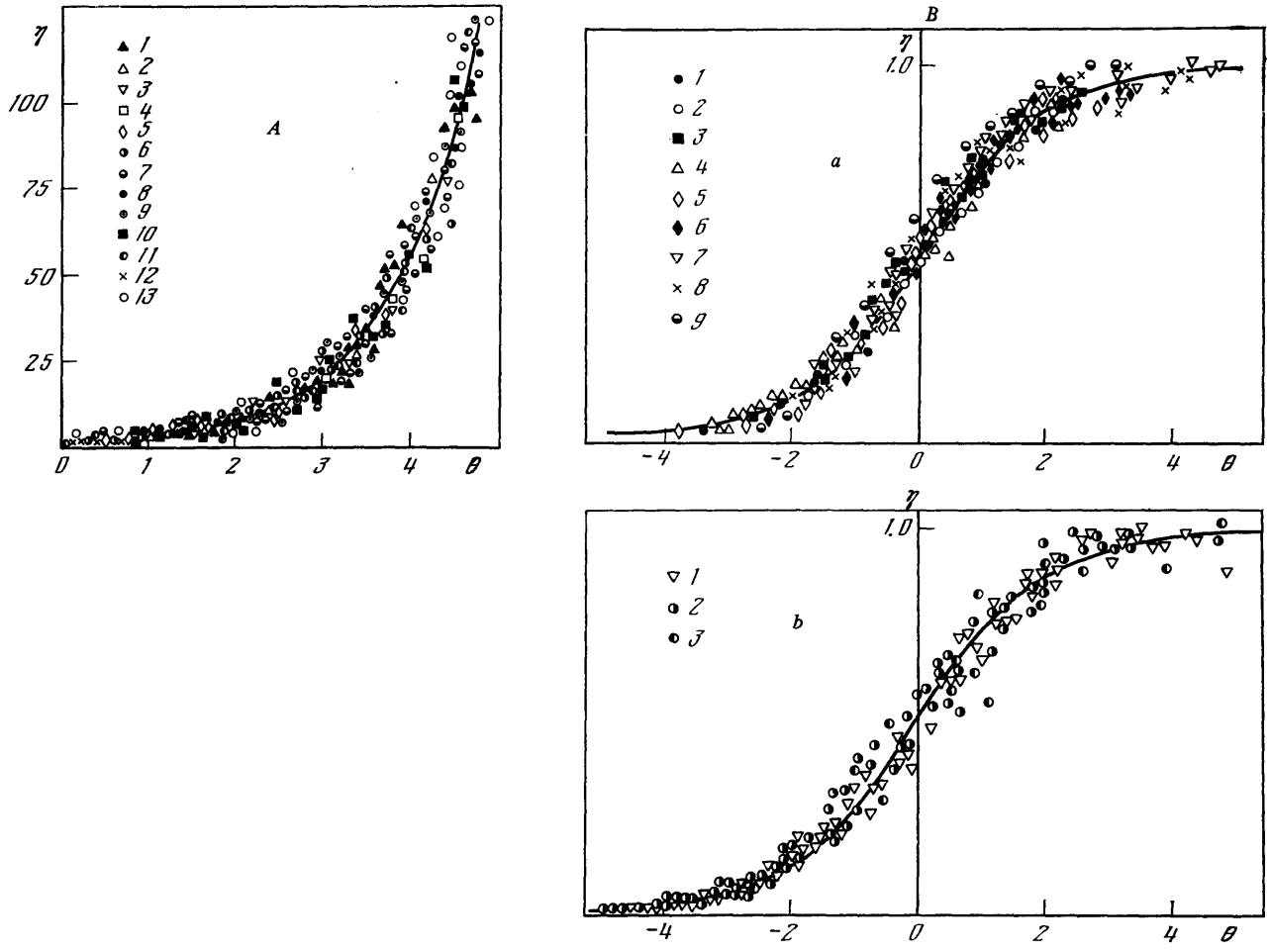


Figure 28. *A*) Generalised kinetic curve for the exponential growth of tumours $\eta = e^{\theta}$ for various types of transplanted tumour processes: 1) tumours in rat skin induced by radiation; 2) adenocarcinoma 755; 3) sarcoma 180; 4) sarcoma CCK; 5) haepatomas; 6) Ehrlich ascites carcinoma; 7) Svec erythromyelosis; 8) Waler carcinosarcoma; 9) reticulosarcomatosis; 10) leukaemia La; 11) leukaemia L-1210; 12) spontaneous leukaemia in mice of AKR strain; 13) leukaemia La; B) generalised S-shaped kinetic curves for the growth of solid (*a*) and ascites (*b*) experimental tumours; *a*: 1) Walker carcinosarcoma; 2) Geren carcinoma; 3) sarcoma 45; 4) adenocarcinoma 755; 5) haepatomas; 6) melanomas; 7) sarcoma 180; 8) other models (osteogenic Ridgeway sarcoma, sarcoma T241, adenocarcinoma EO-771, and carcinoma C1025); 9) Svec erythromyelosis; *b*): 1) sarcoma 180; 2) Ehrlich ascites carcinoma; 3) leukaemia L-1210.[226]

It should be noted that the kinetic criterion κ [Eqn.(105)] for exponentially growing tumours characterises the tumour process much more satisfactorily than the percentage inhibition criterion κ'_9, since κ is the independent of the time of completion of the experiment. The relation between κ and κ'_9 is given by§

$$\kappa_0' = \{1 - \exp[(1-\kappa)\varphi e^{t}]\}1^{0} \quad . \qquad (107)$$

The advantage of the kinetic criterion consists in its high "sensitivity" in the assessment of the most effective preparations. The criterion κ therefore makes it possible to solve one of the main problems of experimental chemotherapy—to establish a relation between the chemical structure and the antitumour activity of the most effective preparations.

§ The numbering of the criteria is based on that in a monograph[226].

Other kinetic criteria, based on the estimation of the average specific rates of tumour growth $\bar{\phi}(t)$, can also be proposed for the estimation of the effectiveness of the antitumour treatment. The average specific rate of growth in the time interval (t_1, t_2) is

$$\bar{\varphi}(t_1, t_2) = \frac{1}{t_2 - t_1}\int_{t_1}^{t_2} \frac{d(\ln F)}{dt}\, dt = \frac{\ln F(t_2) - \ln F(t_1)}{t_2 - t_1} \qquad (108)$$

and, as can be seen from the above equation, depends only on the values of F at the ends of the interval. Thus the quantity $\bar{\phi}(t_1, t_2)$ is equal to the exponent of the "equivalent exponential function", which passes through the ends of the kinetic curve $F(t)$ in the time interval considered.

The ratio of the average specific rates of tumour growth in the control and in the experiment can be adopted as a measure of the effect:

$$\bar{\kappa} = \frac{\bar{\varphi}_c(t_{1c}, t_{2c})}{\bar{\varphi}_e(t_{1e}, t_{2e})} = \frac{t_{2e} - t_{1e}}{t_{2c} - t_{1c}} \cdot \frac{\ln F_c(t_{2c}) - \ln F_c(t_{1c})}{\ln F_e(t_{2e}) - \ln F_e(t_{1e})} \; . \qquad (109)$$

It is natural to adopt the instant t_1 when the therapeutic action begins as the common starting point for reckoning the time intervals (t_{1c}, t_{2c}) and (t_{1e}, t_{2e}) for the averaging. The ends of the time intervals can be chosen in different ways: (a) the ends of the average kinetic curves for tumour growth t_f are adopted as the ends of the time intervals for the averaging, whereupon

$$\bar{\varkappa}_{10} = \frac{\bar{\varphi}_c(t_1, t_{fc})}{\bar{\varphi}_e(t_1, t_{fe})} = \frac{t_{fe} - t_1}{t_{fc} - t_1} \cdot \frac{\ln F_c(t_{fc}) - \ln F_c(t_1)}{\ln F_e(t_{fe}) - \ln F_e(t_1)}\ ; \qquad (110)$$

(b) any instant t_2 at which both kinetic curves to be compared exist can be selected as the common end of the time intervals for the averaging. In this case

$$\bar{\varkappa}_{11} = \frac{\bar{\varphi}_c(t_1, t_2)}{\bar{\varphi}_e(t_1, t_2)} = \frac{\ln F_c(t_2) - \ln F_c(t_1)}{\ln F_e(t_2) - \ln F_e(t_1)}\ . \qquad (111)$$

If the development of the tumour processes in the experiment and in the control proceeds in accordance with exponential laws, then

$$\bar{\varphi}_c(t_1, t_{2c}) = \varphi_c;\ \bar{\varphi}_e(t_1, t_{2e}) = \varphi_e \text{ and}$$
$$\bar{\varkappa}_{10} = \bar{\varkappa}_{11} = \frac{\varphi_c}{\varphi_e} = \varkappa,$$

i.e. the criterion derived previously is obtained.

The fact that the quantities κ_{10} and κ_{11} become infinite following the complete inhibition of tumour growth (at $\bar{\phi} = 0$) constitutes a definite disadvantage (Fig. 29*a*). It is therefore more convenient to employ modified criteria κ^*_{10} and κ^*_{11} which are free from this disadvantage:

$$\varkappa^*_{10} = 1 - \frac{1}{\varkappa_{10}}, \qquad (112)$$

$$\varkappa^*_{11} = 1 - \frac{1}{\varkappa_{11}}\ . \qquad (113)$$

Since both modified criteria are linear functions of the average specific rate of tumour growth in the experiment, i.e.

$$\varkappa^*_{10(11)} = 1 - \frac{1}{\varphi_c}\varphi_e, \qquad (114)$$

the value $\kappa_{10} = \kappa_{11} = 0$ corresponds to the absence of an effect, positive values of κ_{10} and κ_{11} correspond to effective treatment (inhibition of tumour growth), and negative values correspond to treatment stimulating tumour growth (Fig. 29*b*).

The kinetic criterion κ proposed at the Institute of Chemical Physics of the USSR Academy of Sciences in 1962 has been used to investigate the antitumour effectiveness of a large number of chemical compounds of different classes, which made it possible to discover four new highly active preparations: 2,6-di-t-butyl-4-methylphenol (ionol or dibunol), nitrosomethylurea (NMU),[230,231] 1,2-bisdiazoacetylethane (diazan),[232] and PAT-1, a paramagnetic analogue of Thio TEPA.[233] Fig. 30 illustrates the antitumour effectiveness of a series of preparations in relation to the experimental leukaemia La in mice. Under the same "dibunol", ionol is nowadays used in clinical practice in the treatment of the cancer of the bladder and radiation cystitis in man[234] and NMU is used in the treatment of the undifferentiated cancer of the lung, lymphogranulomatosis, and melanoma[231–235].

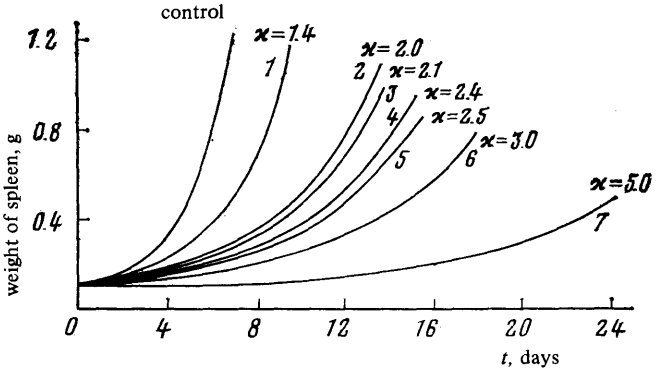


Figure 30. Inhibition of the growth of leukaemia La in mice under the influence of various chemotherapeutic preparations: 1) thiophosphamide, carminomicin; 6) mercapturopurine; 2) sarcolysine; rubomycin; 3) HMM; 4) dibunol, cyclophosphane; 6) PCNU [1-(2-chloroethyl)-3-(2,6-dioxo-3-piperidinyl)-1-nitrosylurea]; 7) diazan.

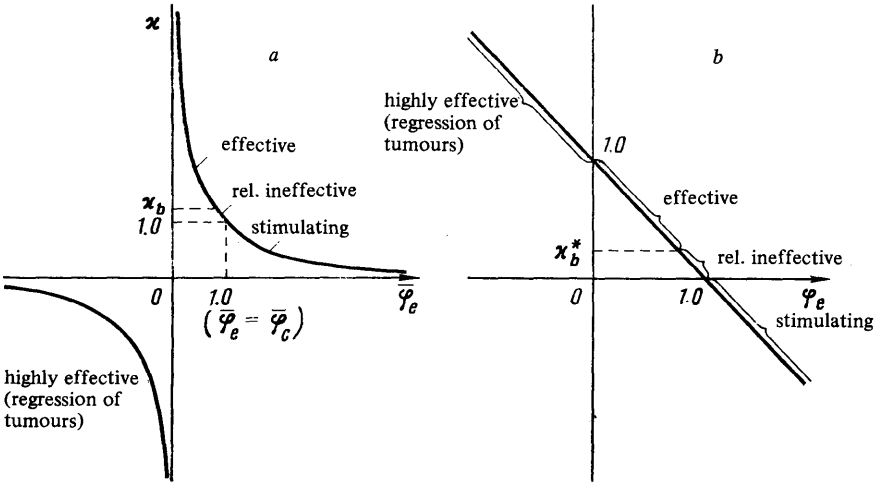


Figure 29. The regions in which therapeutic treatments are effective; $\kappa_b = 1.25$ and $\kappa^*_b = 0.2$ are conventional quantities separating relatively ineffective and effective treatments[226].

The development of kinetic approaches to the description of tumour growth processes in chemotherapeutic treatment is closely related to the problem of the pharmacokinetics of antitumour agents. The parameters of the pharmacokinetic equations are quantitative characteristics of processes involving the entry, distribution, transformation in the organism, and secretion of substances and their estimation makes it possible to relate the intensity of the therapeutic effects to the active concentration of the active forms of the preparation and not to the dose. This permits rational planning of chemotherapeutic regimes[236,237].

3. Kinetics of the Survival of Patients and the Effectiveness of Chemotherapy

The most important and most evident index of the effectiveness of the treatment of malignant tumours is the survival time of the patients. The survival time is a random quantity the statistical characteristics of which are determined by the type and stage of the development of the tumour, the theropeutic regime, and other factors.

Survival can be regarded as the kinetics of the change in the number of living patients determined by the distribution of the survival time in the initial group. The view that survival is a kinetic process makes it possible to apply to it standard mathematical methods adopted in kinetic studies and to obtain a complete quantitative description of survival with the aid of a small number of parameters having a definite physical significance. This is an advantage of the kinetic method over the traditional statistical method in which the percentage survival of patients is estimated solely in relation to a single specific time (for example, the five year survival)[238].

As a result of systematic studies on the kinetics of the survival of patients subjected to radical operations and untreated patients with malignant tumours in different locations, based on observations on several tens of thousands of patients, it has been established that the entire wide variety of forms of kinetic survival curves can be satisfactorily fitted by a small number of simple analytical relations.

If the factual data permit a detailed analysis of the survival curve, it is found that it is as a rule S-shaped. This is due to the unimodality of the corresponding distribution density $f(x)$ of the survival time, since the kinetics of the change in the fraction of surviving patients $P(t)$ are determined by integrating this density:

$$P(t) = \int_t^\infty f(x)\,dt \quad . \tag{115}$$

It has been shown that in many cases this distribution is of the lognormal type[238]:

$$f(x) = \frac{1}{x\sigma\sqrt{2\pi}} \exp\left[-\frac{(\ln x - m)^2}{2\sigma}\right], \quad x > 0 \quad , \tag{116}$$

so that the survival function is

$$P(t) = \frac{1}{\sqrt{2\pi}} \int_{\frac{1}{\sigma}\ln\frac{t}{T}}^{\infty} e^{-x^2/2}\,dx \quad , \tag{117}$$

where T is the median of the survival and σ^2 is the variance. The survival of patients suffering from cancer of the stomach, the mammary gland, the neck of the uterus, the lung, the mouth and the pharynx, and the tongue, as well as bone tumours can be described in terms of this relation.

In cases where clinical data are insufficiently detailed, it is useful to use a simpler one-parameter family of functions. Families of exponential and hyperbolic functions have been used for this purpose. In the first case the survival function is of the form $P(t) = e^{-kt}$ and describes, for example, the survival of patients with cancer of the stomach. In the second case the survival function is of the form $P(t) = 1/(a + kt)$; this case refers to cancer of the lung, the mammary gland, the rectum, the kidney, and the bladder.

It was shown that each location of the tumour is characterised by its own type of kinetic survival curve, which is the same for different hospitals and different times and is determined solely by the type of tumour[238]. This makes it possible to compare the effectiveness of different methods of treatment by comparing the different kinetic parameters.

Analysis of the influence of various clinical-morphological factors on the parameters of kinetic survival curves established that, for each type of tumour, the spread (stage) of the tumour process at the instant of diagnosis or the beginning of treatment plays the main role. The remaining factors such as sex, age, histological structure of the tumour, etc. are secondary.

The parameters of the functional relations for survival can be estimated along a comparatively short section of the kinetic curve, for example from data for the first 2–3 years of observation on patients subjected to a radical treatment or the first 3–6 months for non-operable patients. Knowing these survival constants, it is possible in its turn to extrapolate the kinetic curve to longer times and thus obtain a prognosis of survival at any time. Such prognosis is extremely important for practical medicine, since it makes it possible to accelerate the assessment of the effectiveness of new methods of treatment of malignant tumours. The observed 5–10 year survival of patients subjected to radical operations for cancer of the stomach, the lung, the mammary gland, the rectum and the large intestine, the kidney, and the bladder hardly differs from the calculated values obtained from data for 2–3 year survival.

The availability of stable kinetics relations for each type of tumour makes it possible to apply standard statistical procedures and to obtain estimates of the parameters for the general set of survival data for patients with tumours of a particular type. The analytical relations used to describe the factual data can be linearised in terms of appropriate coordinates and their parameters can be estimated by the method of linear regression. Such estimates have been obtained for patients who have undergone a radical operation for cancer of the stomach, the lung, the mammary gland, the bladder, and the rectum and for non-operable patients with cancer of the stomach and the lung[238].

These results have served as a theoretical and methodological basis for the development of a kinetic method for comparative estimates of the effectiveness of treatment in which the enormous amount of information accumulated in various clinics in the world is used as the "historical" control. The method makes it possible to abandon the simultaneous establishment of special control groups of patients and significantly accelerates the study of new medicinal compounds and the practical application of the most effective preparations.

As an example of the practical application of this method, Fig. 31 presents survival data from 33 clinics, generalised with the aid of the kinetic method, for patients with inoperable cancer of the lung who had not been subjected to a special treatment ("historical control") and survival data for 168 similar patients receiving chemotherapy. Fig. 31 shows that data for the 3 and 6 months survival of patients for whom a direct improvement was observed after chemotherapy (the majority of the patients were treated with nitrosomethyl-

urea) lie outside the 95% confidence zone of the "control". On the other hand, the survival of patients in which there was no improvement after treatment did not differ from the control. Thus kinetic analysis made it possible to observe that the use of prepations leading to a direct improvement of patients with cancer of the lung reliably increases their survival time, but the improvement is so far restricted to only 6 months.

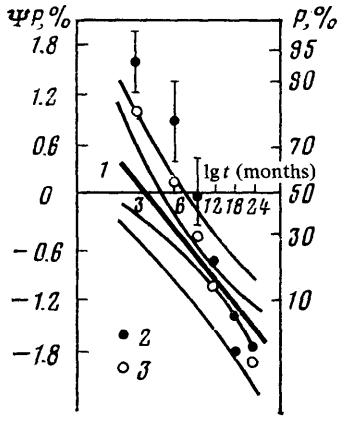


Figure 31. 1) Generalised survival curve for patients with inoperable lung cancer who have not been receiving chemotherapy, calculated from data from 33 clinics by the method of linear equation and transformed into a plot in terms of logarithmic statistical coordinates. The circles denote data for patients receiving chemotherapy: 2) cases involving improvement; 3) remaining cases[240].

The survival of patients is evidently closely related to the nature of the growth of the corresponding type of tumour, so that the study of this relation makes it possible to estimate from survival data parameters of tumour growth which cannot be derived by direct measurements[239].

A mathematical model relating to the survival of patients to the rate of growth of the mass of the tumour has been developed. The following expression has been obtained for the survival time:

$$t_m = \tau\gamma(V_0, V_m) \ , \qquad (118)$$

where τ is the time required for the doubling of the volume of the tumour and γ the coefficient of growth which depends on the nature of the growth of the tumour and on the rate of the initial (V_0) and final (V_m) masses.

The model makes it possible to estimate the mass of the tumour in the organism for different extents of the tumour process. It has been shown, for example, that the organisms of patients subjected to radical operations for cancer of the stomach without regional metastases, who subsequently died from the tumour, contained after the operation on average 10^7–10^8 residual tumour cells, while in non-operable patients there are 10^{11} tumour cells, etc. Such data can probably be used in the planning of the therapy of patients with different extents of the process.

Subject to the condition that the increase in survival as a result of treatment of the tumour (irradiation or chemotherapy) is due to the destruction of a specific proportion of tumour cells, the model makes it possible to estimate this fraction from survival data, i.e. to estimate the factor by which the treatment reduces the mass of the tumour. As an example, Fig. 32 presents kinetic curves for the survival of patients subjected to radical operations for cancer of the lung. For some patients, the treatment was confined to the operation, while others were given an additional chemotherapy with cyclophosphane [data from the Gertsen Moscow Institute of Oncology (MNIOI)]. Evidently the combined treatment led to an improvement of survival.

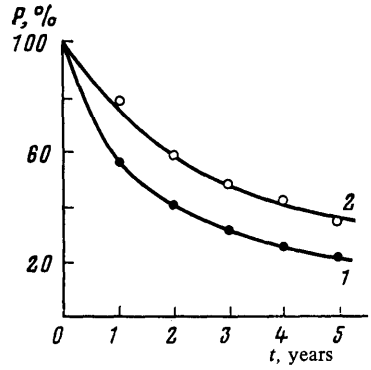


Figure 32. Kinetic survival curves for patients after radical operations for lung cancer; 1) surgical treatment alone; 2) chemotherapeutic treatment after operation [240].

According to the model, the decrease of the mass of the tumour as a result of the additional treatment is defined by the expression

$$\ln\frac{V'}{V} = \gamma\left(1 - \frac{T'}{T}\right) , \qquad (119)$$

where V and V' are the average masses of the tumours in patients belonging to the groups being compared and T and T' are the medians of the survival times of the patients in these groups.

The calculations showed that in the example presented in Fig. 32, the increase of survival was a result of the decrease of the mass of the tumour by a factor of 400 (the average for the group considered). This can be regarded as a quantitative index of the effectiveness of cyclophosphane in the combined treatment of cancer of the lung.

Similar parameters can be used also for comparative estimates of the effectiveness of different preparations.

4. Application of Factorial Analysis in the Quantitative Estimation of the Joint Action of Combined Preparations

The greatest effect in the chemotherapy of cancer is usually attained when two and more antitumour preparations are used. In practice optimum chemotherapeutic regimes are chosen empirically at the present time. The number of possible combinations is then extremely large and it is difficult to count on finding the objectively optimum regime. The possibility of a rigorous determination of the mutual influence of the preparations as a basis for the optimisation of combined chemotherapy then becomes particularly important.

The method of factorial analysis was used for the first time to assess quantitatively the joint action of diazan and cyclophosphamide in the treatment of leukaemia R-388.[232] This made it possible to determine the contribution of each preparation (factor) to the overall final result of the therapy and also to find a quantity characterising the interaction of the factors (λ).

The effectiveness and interaction of the factors can be expressed in an analytical form by the equation

$$\lambda_{k_1 k_2} = \sum_{l=1}^{m} \left\{ (-1)^q \sum_{i=1}^{m} \tau_{ij} \right\}, \qquad (120)$$

where $k_1 = 1, 2, \ldots, l$, $k_2 = 1, 2, \ldots, l$, $q = 1$ or 2, and τ_{ij} is the lifetime of the animal.

The application of factorial analysis led to the discovery of different degrees of therapeutic synergism for identical activity indices of the preparation. In Fig. 33 the experimental results are presented in the form of equieffective curves. A point in the plane represents the results of the combined action of two preparations taken in specific doses. The numerals in the graph represent the activity coefficients. By interpolating the values of the effectiveness on the basis of the experimental points, it is possible to calculate the values for other points and then to plot curves on which each point corresponds to the same effectiveness. Fig. 33 presents equieffective curves of κ ranging from 2 to 6.

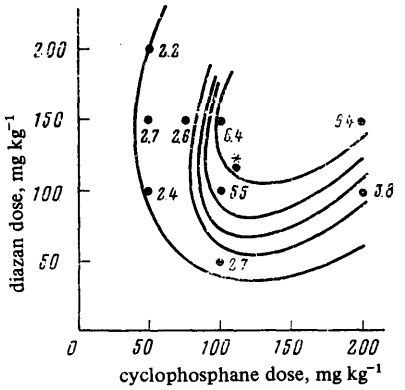


Figure 33. Equieffective curves for the combined treatment with diazan and cyclophosphane calculated for κ ranging from 2 to 6.[240]

The equieffective curves make it possible to determine the region of the maximum effectivness and to estimate the optimum treatment, i.e. to determine the minimum doses of the preparation sufficient to achieve the maximum effect. Evidently the point (represented by an asterisk) at which the diazan dose is 120 mg kg^{-1} and the cyclophosphane dose is 110 mg kg^{-1} corresponds to these conditions. Indeed subsequent experiments showed that the maximum effectiveness of the treatment is then observed.

This approach to the analysis of the results of polychemotherapy leads to the possibility of rigorously justified clinical recommendations and permits the solution of the problem of optimising combined therapy.

5. Classification of Antitumour Preparations in Terms of the Principle of Chemical Reactivity

The synthesis of substances with antitumour properties specified beforehand constitutes an insignificant fraction of the enormous amount of research throughout the world into the synthesis of new chemical compounds. To some extent, this is a consequence of traditional self-limitations, as a result of which the search for new effective antitumour preparations is usually prosecuted within the limits of a few empirically discovered classes of chemical compounds such as alkylating agents, antimetabolites, antibiotics, and hormonal preparations.

In terms of the mechanism of their action, these substances can be divided into two main groups—compounds characteristic of the metabolic processes in normal or tumour cells or derivatives similar to such compounds (biochemically functionally active compounds) and substances for which a purely chemical interaction with the cell molecules plays the main role (chemically functionally active substances).

A condition for the most effective application of the antitumour preparations of both groups is in most cases a natural or artificially created enhanced sensitivity of tumour cells to the action of preparations relative to normal cells.

Biochemically functionally active preparations. Enzymes (L-aspartase and ribonuclease), hormones (cortisone, prednisolone, testosterone, and diethylstilboestrol), certain metabolites from a series of membrane-active regulators of metabolic processes and structural analogues of metabolites—the antimetabolites of nucleic acid exchange (mercaptopurine, thioguanine, 5-fluorouracil, ftorafur, 5-azacytidine, etc.), and antimetabolites of folic acid metabolism (methotrexate and aminopterin) should be included among biochemically functionally active antitumour compounds.

It is possible to discover new effective preparations among biochemically functionally active substances. This is indicated particularly by the unexpectedly successful application in tumour chemotherapy of synthetic analogues of bioantioxidants—ionol, ambunol, etc.

Chemically functionally active compounds. It is known that the total number of specific substances with which chemists have dealt for one reason or another is almost ten million in the field of organic chemistry alone and there are no fundamental difficulties in multiplying this number by a large factor.

The classification of antitumour preparations generally adopted at the present time is based on several different principles: the mechanism of biological action (antimetabolites and hormones), the source (antiobiotics, alkaloids, and enzymes), and chemical properties (alkylating agents). Synthetic preparations the mechanism of whose action has not yet been established constitute a large group, which is not in fact included in the above classification. Such classification of the antitumour preparations is inadequate as a basis for the rational planning of the synthesis of new preparations or for the selection of potential antitumour agents from the enormous number of chemical compounds known at the present time. Furthermore, from a purely chemical standpoint, it is possible to put forward a more systematic classification based on the types of structures and the types of chemical reactivities of these compounds[240]. Indeed they can all be divided into five main groups in terms of their characteristic reactions:

(1) electrophilic reactions;
(2) free-radical reactions;
(3) complex formation reactions;

(4) nucleophilic reaction;
(5) cycloaddition.

In this section the chemical structures and mechanisms of the action of antitumour agents will be considered from the standpoint of the classification based on this principle.

(1) Electrophilic reactions. In the modern arsenal of effective antitumour agents the greatest proportion consists of chemical compounds reacting via the mechanism of electrophilic interactions, which include the formation of electrophilic species (carbonium ions which alkylate or acylate the nucleophilic centres of principal chemical components of the cell).

β-Chloroethylamines, β-chloroethyl sulphides, epoxides, aziridines, sulphonate and phosphate esters, halogenomethyl ketones, chloromethyl ethers, ammonium and sulphonium compounds, β-lactones, diazoketones, and nitrosocarbamides behave as alkylating agents *in vivo*.

Table 11. Alkylating agents.

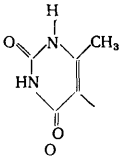
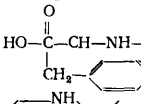
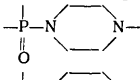
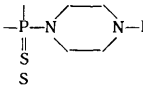
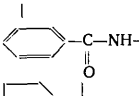
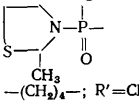
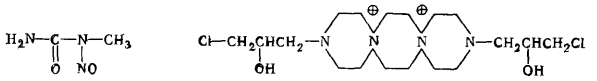
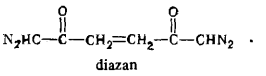
Overall formula	Carbonium ions	Name of preparation	R
$R-N(CH_2CH_2Cl)_2 \rightarrow [R-N(CH_2\overset{\oplus}{C}H_2)(CH_2CH_2Cl)]$		embichin	CH_3-
		chlorobutin	$HO-C(=O)-(CH_2)_3-C_6H_4-$
		sarcolysine	$HO-C(=O)-CH(NH_2)-CH_2-C_6H_4-$
		dopan	
		lofenal	$HO-C(=O)-CH(CH_2-)-NH-C(=O)-CH_2-C_6H_4-$
		cyclophosphane	
		dipin	
		thiodipin	
$R-N(CH_2)_2 \rightarrow [R-NH-CH_2\overset{\oplus}{C}H_2]$		thiophosphamide	$-P(=S)-$
		benzotef	
		imiphos	
$R-S(=O)_2-OCH_2R' \rightarrow [R'-\overset{\oplus}{C}H_2]$		myelosan	$-(CH_2)_4-$; $R'=CH_3$
$R-C(=O)-CHN_2 \rightarrow [R-C(=O)-\overset{\oplus}{C}H_2]$		azaserine	$HOOC-CH(NH_2)-CH_2-O-$
		DON	$HOOC-CH(NH_2)-CH_2-CH_2-$
		diazan	$-CH_2-CH_2-$
		nitroso-methylurea	$-CH_3$
$R'HN-C(=O)-N(NO)-R \rightarrow [R^{\oplus}]$		CCNU	$-CH_2CH_2Cl$; $R' =$ 
		BCNU	$-CH_2CH_2Cl$; $R' = -CH_2CH_2Cl$

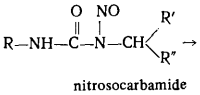
Table 11 presents the structures of the compounds encountered most frequently in practice and of the carbonium ions formed from them. Further progress in the synthesis of antitumour preparations with an alkylating activity is associated with the finding of new types of cytotoxic groups and also with the modification of transport fragments ensuring the selectivity of the action of the preparations. New effective antitumour preparations have been synthesised recently: nitrosomethylurea containing the functionally active nitrosocarbamide group[231], prospidin in which a spiro-heterocycle with quaternary nitrogen atoms serves as the carrier of the bis-β-chloroalkylamino-group[241], and 1,2-bisdiazoacetylethane (diazan) containing two diazoacetyl fragments[226]:

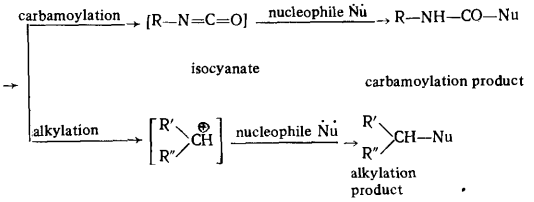

nitrosomethylurea

prospidin

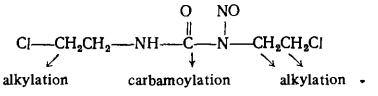

diazan

Nitrosomethylurea, proposed in 1964 as an antitumour preparation, and its homologues and analogues exhibit a dual electrophilic reactivity, in contrast to other alkylating agents, involving not only an alkylating activity but also a carbamoylating activity, which is responsible for the characteristics of the mechanism of the biological activity of compounds of this class:


nitrosocarbamide



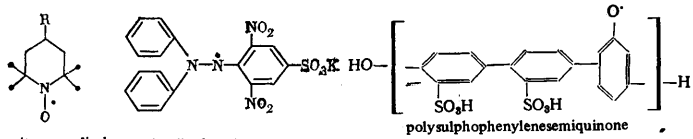
Chloroethylamino-derivatives of nitrosocarbamides contain several reaction centres, in particular the familiar preparation BCNU has a single carbamoylating centre and three different alkylating centres:



Prospidin also contains two types of alkylating centres—the ammonium and chloroalkyl groups. The ionic centres of spiro-heterocycles ensure the specific binding of the preparation to the chemical components of the cell. Prospidin is used in the treatment of cancer of the larynx, retinoblastomas, papillomatesis of the upper respiratory tract, and Kaposi's angiosarcoma[242].

(2) Free-radical reactions. Free-radical reactions constitute an appreciable proportion of the chemical processes occurring in living systems. It is therefore to be expected that compounds capable of being involved in these processes—stable radicals and antiradical agents (inhibitors)—should exhibit a physiological activity.

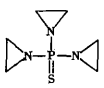
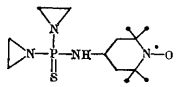
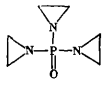
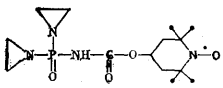
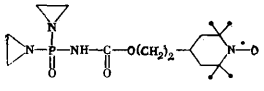
The antitumour effect of stable free radicals was first observed by ourselves in 1964 for nitroxy-radicals and triarylhydrazyls[243] and then for polysulphophenylenesemiquinone[244]:



The radiosensitising effect of nitroxy-radicals has also been demonstrated[225].

The use of stable radicals for the structural modification of certain known antitumour preparations is extremely promising. The paramagnetic derivatives of thiophosphamide, phosphamide, and triethylenemelamine synthesised and investigated at the present time are characterised by a toxicity lower by more than an order of magnitude than that of the initial compounds, while retaining the same or even higher antitumour activity (Table 12).

Table 12. The antitumour activities of paramagnetic analogues of antitumour agents[240].

Formula	LD_{50}^{a}, mg kg^{-1}	Δ^{b}, % (leukaemia La)	x^{c} (leukaemia La)	Inhibition of tumour growth^{b}, %			
				WCS	SEM	EAC	S-180
 Thiophosphamide	18	20	0.3	100	100	45	—
	187	80	0.5	100	100	70	50
 Phosphamide	15	—	—	65	—	50	—
	150	170	1.0	100% inhibition of tumour growth			
	280	80	0.4	100% inhibition of tumour growth			

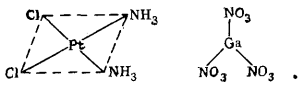
Notation: *a*) dose of the preparation for which 50% of the animals die due to its toxicity; *b*) increase of the average lifespan of the animals; *c*) WCS = Walker carcinosarcoma 256; SEM = Svec erythromyelosis; EAC = Ehrlich ascites carcinoma; S-180 = sarcoma 180.

The synthesis of chemically polyfunctional antitumour preparations, incorporating a stable nitroxy-radical as the carrier of the alkylating group, leads to a fundamentally new type of preparations with a combined mechanism of action, which combine the properties of substances with electrophilic reactivity and substances undergoing free-radical reactions.

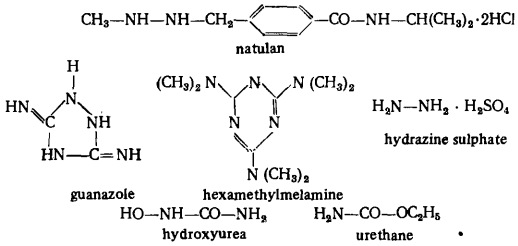
(3) Complex formation. Complex-forming agents capable of donor–acceptor interactions of various types (the formation of charge-transfer complexes, hydrogen bonding, hydrophobic interactions, and the formation of metal complexes) constitute a large and structurally varied group of antitumour preparations. Many antibiotics, which combine with the nitrogen-containing DNA bases as intercalating agents (antibiotics of the anthracycline [anthramycin? (Ed.of Translation)] series—adriamycin, rubomycin and carminomicin, antibiotics belonging to the aureolic acid group—olivomycin and mithramicin, as well as actinomycins) should be assigned to this group. The intercalation mechanism can be proposed for many polycyclic compounds and ionic forms of polyheterocycles (phenothiazines, phenoxazines, and acridines).

Metal salts and complexes (gallium nitrate and platinum group metal complexes) constitute a special group of antitumour preparations. The mechanism of their biological action is due to their ability to combine with information biomacromolecules. This field of tumour chemotherapy has in essence only begun to develop.

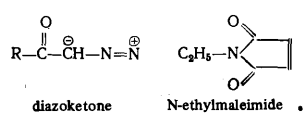
In the future one may expect the synthesis of new antitumour preparations consisting of a series of mononuclear and dinuclear complexes of various metals:



(4) Nucleophilic reactions. Nucleophilic reactions have not been considered at all in the literature as reactions of importance from the standpoint of the antitumour effect. Nevertheless the electrophilic centres of metalloenzymes (carbonyl and azomethine groups) can serve as targets for preparations with nucleophilic reactivity. Indeed, among antitumour preparations classified as substances with different (or even unelucidated) mechanisms of action, it is possible to distinguish derivatives of hydrazine, carbamide, and nitrogen-containing bases which are strong nucleophiles:



(5) Cycloaddition. Direct data indicating the possibility of cycloaddition reactions in the organism involving antitumour preparations are not at present available. However, the presence of activated double bonds in many metabolites does not rule out the Huisgen or Diels–Alder reactions. *N*-Ethylmaleimide and diazoketones can be included among antitumour agents capable of participating in these reactions:



The new classification of preparations in terms of types of reactivity, which the present author proposed, is more general than the traditional classification, permits a more

detailed treatment of the chemical and biochemical mechanisms of the action of antitumour preparations, and provides a basis for the rational planning of their synthesis. Preparations with hybrid structures and correspondingly with hybrid reactivities fit satisfactorily within the framework of this classification.

6. Correlation between the Chemical Structure and the Antitumour Activity of Compounds

Quantum-chemical calculations can be used to predict the biological activity and to select the optimum structures of antitumour preparations. Among the many methods for the determination of quantitative relations between the structures of compounds and their biological activities, those of Free and Wilson[245] and Hansch and Deutsch[246] are most widely used. The Hansch equation makes it possible to establish a correlation between the biological activity A and the physicochemical characteristics of the substance:

$$\lg A = \rho\sigma + \alpha\pi + \gamma E_s + B \,, \qquad (121)$$

where σ characterises the polar effects in the molecule (in particular it can be Hammett constants or quantum-chemical characteristics of the electronic structure), E_S are steric factors (for example Taft constants), and π represents the distribution of the preparation in the lipid–water system ($\pi = \lg P$, where P is the partition coefficient in the 1-octanol–water system). The polar factors σ depend on the distribution of electron density in the molecule and on the free valence indices of the reactive atoms, which determines in its turn the chemical reactivity of the molecule as a whole.

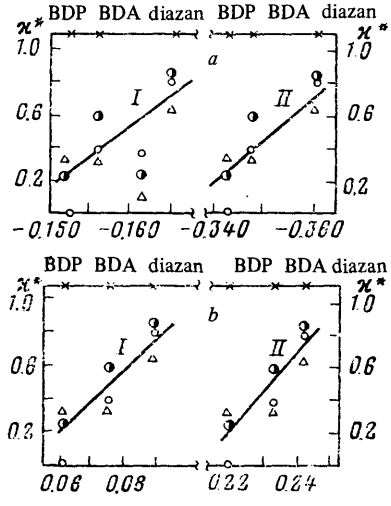


Figure 34. Correlation between the negative charges (*a*) and free valence indices (*b*) of the oxygen atoms (I) and carbon of the methine group (II) and the antitumour activity κ^* in a series of bisdiazoketones; BDD = bisdiazoacetyl; BDP = bisdiazoacetylpropane; ○—Ehrlich ascites carcinoma; ◑—leukaemia La; △—sarcoma 180.[240]

Quantum-chemical calculations of the structure of bisdiazoketones by the semiempirical CNDO/2 method[247] showed that a change in the electron-donating properties of the substituents influences significantly the distribution of electron density in the diazoketone fragment. It was found that the antitumour effect is correlated with the charges on the C and O atoms and the Wiberg indices and also with the Hammett constants σ and the energies of the highest occupied molecular orbitals E_{HOMO} and the lowest unoccupied molecular orbitals [E_{LUMO} (Fig.34)].

7. Free Radicals and Tumour Growth. Inhibitor-antioxidants as Anticarcinogenic and Antitumour Preparations

A little more than two decades ago, the author put forward ideas concerning the possibility of biophysical shifts associated with changes in the content of free radicals in tissues in various pathological states (malignant growth, radiation damage, and the effect of toxic substances).

Paramagnetic centres—free radicals (FR) and transition metal complexes (Mn, Fe, Mo, etc. complexes)—have now been detected in many tissues of animal and plant organisms functioning normally and their nature has been determined. Fig.35 illustrates the characteristic EPR spectrum of liver cells. The narrow EPR singlet with a g-factor of 2.003¶ corresponds to free radicals of the semiquinone type, observed in many other organs and tissues. Mainly flavins in the semioxidised state and the semiquinone form of ubiquinones, functioning as electron transferring agents in the respiratory and energy chains of mitochondria, are responsible for this signal.

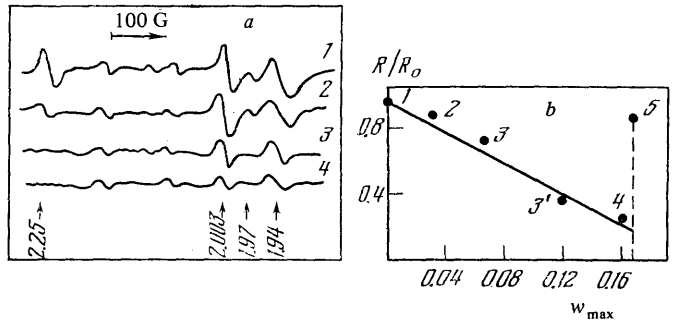


Figure 35. Paramagnetic centres in tissues of normal liver and in transplanted haepatomas: *a*) EPR spectra of frozen specimens of normal liver tissue (*1*), haepatoma 46 showing a minimal deviation (*2*), rapidly growing haepatomas 60 and 22a (*3* and *4*); *b*) relative content of free radicals in normal ($R/R_0 = 1.0$) and regenerating livers (*5*) and also in haepatomas with different rates of growth[226].

The EPR signal of flavin radicals in tissues has a half-width of 14–15 G,[248,249] and for ubiquinone radicals $\Delta H = 10$–11 G.[250] Depending on the ratio of the amounts of flavin, ubiquinone, and other free radicals, the EPR signal half-width for the tissue can vary from 10 to 16 G.

The signal with $g = 1.94$ is due to iron sulphur complexes in mitochondria. The haem iron of cytochrome P-450 in microsomes in a low-spin state gives rise to an anisotropic signal with $g = 1.91$, 2.25, and 2.42; the component with

¶ In certain studies a different value of the g-factor of the free radical signal has been reported (up to 2.005).

g = 2.25 is most intense. A signal with g = 1.97, due to molybdenum compounds of xanthine oxidase and sulphate redutase, can also be observed.

It is natural to expect that, in the development of pathological processes in the organism, the content of free radicals and other paramagnetic centres can differ from the norm and that EPR signals not characteristic of the organism under normal conditions may appear. Indeed, in many pathological processes such as radiation damage, cancer, virus diseases, and various stresses on the organism (hypoxia, hyperoxia, etc.), the content of free radicals (g = 2.003) and other paramagnetic centres in the tissues changes and new signals appear, for example, a signal with g = 2.03 [251–253] and a triplet signal with the centre at g = 2.007.[254,255]

A quantitative relation has been observed between the intensities of individual signals in the EPR spectra and the level of metabolic activity of the tissues[256]. This served as a basis for the study of the kinetics of the change in the paramagnetic properties of organs and tissues in carcinogenesis and tumour growth. The change in the content of paramagnetic centres in the tumour is one of the physicochemical characteristics of tumour growth.

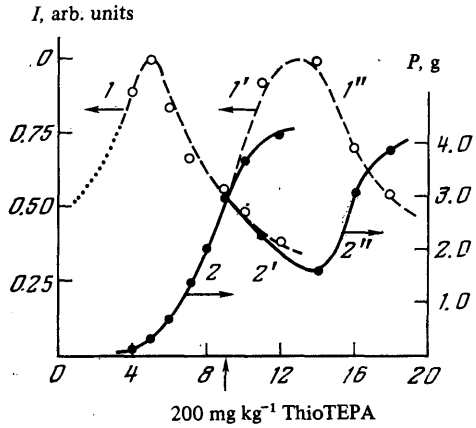


Figure 36. Variation of the content of free radicals (curves *1*, *1'*, and *1''*) in tumour tissue and of the weight of the tumour (curves *2*, *2'*, and *2''*) in the course of growth (curves *1* and *2*), regression (curves *1'* and *2'*), on treatment with ThioTEPA (200 mg kg^{-1}), and relapse (curves *1''* and *2''*) of adenocarcinoma 755 in mice. The arrow indicates the instant of administration of ThioTEPA (I = amplitude of signal with g = 2.00 in EPR spectrum).

In all cases (approximately 25 experimental tumours) the kinetic curves for the variation of the content of free radicals in the tumour passed through a maximum near the point of the maximum tumour growth[257]. As an example, one may consider curve *1* in Fig.36, which reflects the characteristics of the variation of the number of radicals in an experimental tumour (adenocarcinoma 755) on the 4th–12th day of its development (the EPR spectra were measured at 77 K). Taking into account the concentration of radicals in the tumour tissue on the 9th day, when the tumour was transplanted, one may postulate that in the first three days after transplantation the content of free radicals increases (shown by circles) up to the maximum values observed on the 4th–5th day. Evidently the maximum in the kinetic curves for the variation of the content of radicals is determined by consistent biophysical changes in malignant growth. The content of free radicals in developing tumours is appreciably below the norm (sometimes by a factor of 2–3).

The process of the development and growth of a malignant tumours induces specific biochemical changes in various organs and tissues of the animal tumour carrier. In particular, the decrease of the functional activity of the liver in the course of the growth of transplanted tumours is reflected in a decrease of the concentration of paramagnetic metal complex and free radical centres relative to the norm. It has been shown for six types of experimental transplanted leukaemias that the content of radicals in the livers of mice remains at the normal level in the course of the latent period of the development of the leukaemic process and then falls[258].

In the chemotherapy of tumours the EPR spectra of tumour cells and the organs of tumour carriers shown an increase of the intensity of EPR signals corresponding to the magnitude of the antitumour effect. Such data have been obtained, for example, when leukaemia La was treated with diazan, haepatoma 46 was treated with dibutyryl-cAMP, and melanoma B-16 was treated with thiophenosphamide. The observed increase of signal intensity in the EPR spectra under these conditions is probably associated with the growth of the metabolic activity of the tissues.

In the chemotherapy of adenocarcinoma 755 with cyclophosphane an increase of intensity (by 30–40%) and of the half-width of the free radical signal (from ΔH = 10 G to ΔH = 12–13 G) was observed in the tumour regression stage, while in the subsequent recovery of the tumour the opposite effect was noted (see Fig.36). This can be accounted for by changes in the ratio of the paramagnetic forms of flavin and ubiquinone and their different contributions to the measured EPR signal of the tumour tissue[259]. An analogous result was obtained also under clinical conditions: in the therapy of cancer of the rectum the decrease in the size of the tumour was accompanied by an increase of the intensity of the EPR signal of the free radicals in the specimens.

Thus the study of the kinetics of the changes in the paramagnetic properties of tissues can be used to investigate the development of tumours and to assess the effectiveness of the therapy.

Free-radical shifts have also been observed in kinetic studies of the paramagnetic properties of animal tissues in the course of chemical carcinogenesis. Fig.37 shows that complex multistage changes in the content of free radicals take place in rat livers in the course of the malignant degeneracy under the influence of diethylnitrosamine (DENA).[251] Analogous curves have been obtained in the carcinogenesis under the influence of other carcinogens: dimethylaminoazobenzene (DAB),[260] 3,4-benzopyrene[261], and Teflon[262].

The study of the kinetics of the variation of the concentration of radicals in tissues and cells in the course of viral, chemical, and spontaneous carcinogenesis made it possible to observe many common features, despite the different nature of the agents inducing this process, and to put forward hypotheses concerning the nature of these shifts. The most characteristic feature is a maximum on the curves for the content of free radicals in tissues in the initial period of carcinogenesis regardless of the species, sex, and age of the animals, the type of cells undergoing malignant degeneracy, and the experimental conditions.

An analogous maximum in the content of radicals in liver tissues has been observed when animals were treated with non-carcinogenic toxic substances—benzene, DDT, and oxidised sunflower oil (Fig.37*b*). Evidently the observed maximum is associated with a non-specific response of the organism to the introduction of the toxic compound.

The free-radical shifts observed in animal livers and also brains under the influence of toxic substances can serve as a measure of the influence on the organism of particular agents in the environment.

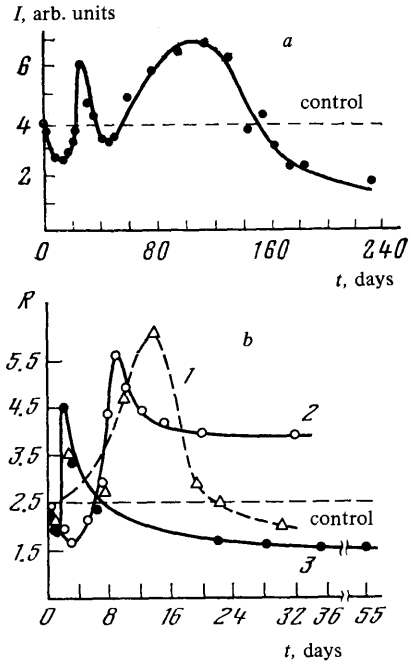


Figure 37. Variation of the content of free radicals (g = 2.003) in rat liver in carcinogenesis induced by diethylnitrosamine (a) and under the influence of toxic agents (b):[226] 1) oxidised sunflower oil; 2) benzene; 3) DDT.

The ideal of a significant role of free-radical shifts in tumour growth and carcinogenesis served as a basis for the hypothesis that inhibitors with a low toxicity which suppress the development of radical processes can prove to be effective anticarcinogenic agents. Numerous experiments have shown that the familiar inhibitor of radical processes and antitumour preparation 2,6-di-t-butyl-4-methylphenol (dibunol) does indeed exhibit an effective anticarcinogenic activity. Rat liver tumours have been induced by including dimethylaminobenzene (DAB) in the diet[263]. Under the influence of DAB, tumours arose in 90% of the animals after 90 days. When 0.3 wt.% of ionol was added to the food together with the carcinogen, tumours did not develop even after treatment with DAB for 150 days. Pre-tumour changes in the animal livers were completely absent.

The anticarcinogenic activity of radical process inhibitors which we established was confirmed by other workers[264,265].

We have investigated the molecular aspects of this extremely important problem[260]. We observed that the introduction of ionol together with the carcinogen prevents an increase of the concentration of free radicals in the initial stage of the action of the carcinogen, maintaining it at a level close to that in the normal liver tissue (Fig.38). Tumours did not arise in the course of twelve months of observation in animals receiving 2,6-di-t-butyl-4-methylphenol.

The experimental data obtained give rise to the problem of the development of methods for the prophylaxis of malignant diseases.

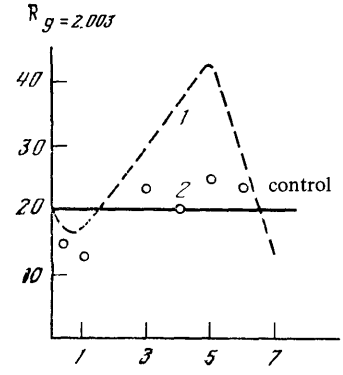


Figure 38. Variation of the concentration of free radicals in rat liver under the influence of DAB (*1*) and under the joint influence of DAB and ionol (*2*).[226]

8. The Antioxidant Activity of Lipids in Normal and Tumour Tissues and Chemotherapy

Approximately two decades ago, the concept of the antioxidant activity (AOA) of tissue lipids, characterising the involvement of bioantioxidants in metabolic processes, was introduced into biochemistry[266].

The value of AOA (in ml h g^{-1}) is determined from the ability of lipid fractions to inhibit the oxidation of a standard substrate, for example, methyl oleate, which is oxidised at a rate suitable for measurement even at physiological temperatures:

$$(\mathrm{AOA}) = \frac{\tau - \tau_{\mathrm{stand}}}{P} \quad , \qquad (122)$$

where τ and τ_{stand} is the time of attainment of the same degree of oxidation of the substrate with the lipid fraction and of a standard substrate and P is a sample of the lipid fraction. The quantity AOA is extremely sensitive to various normal physiological and pathological states of the organism and also to the action of physical and chemical factors.

The growth of transplanted tumours is accompanied by a change in the AOA of the lipid fractions of the tissues and organs of animal tumour carriers and in the tumour tissues formed compared with the norm (for organs) and with the initial value of AOA for the transplanted material[267,268]. This change passes through an extremum as a function of the time of development of the tumour process. In successful chemotherapy the retardation of tumour growth is accompanied also by the retardation of the increase of AOA. This can be used for monitoring the course of the therapy.

The study of the changes in AOA in animal tissues under the influence of chemical and physical factors leads to important conclusions. All the effective antitumour preparations reduce AOA compared with the normal level after administration to healthy animals[269] (Fig.39).

This effect is observed for all alkylating compounds and synthetic antioxidants when they are administered in doses ensuring the antitumour activity of hormones and antimetabolites. In the case of hormones the suppression of AOA after a certain time is replaced by an increase of AOA to which corresponds an acceleration of tumour growth in chemotherapeutic experiments. However, repeated administration of these preparations, ensuring the maintenance of the AOA level below the norm, results in the retention of the antitumour activity. These observations are fully consistent with clinical data concerning the application of hormones and antimetabolites as antitumour agents. Non-specific influences such as irradiation with X-rays and stress also cause a decrease of AOA and the corresponding antitumour effect.

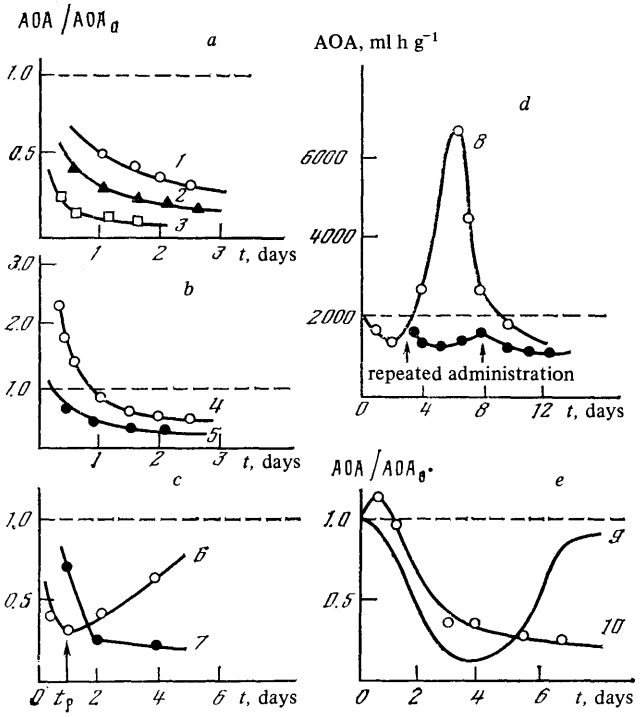


Figure 39. The influence of various preparations [*a*) alkylating agents; *c*) antimetabolites; *d*) hormones; *e*) physical factors] on the AOA of the lipids in the livers of healthy animals: 1) ThioTEPA; 2) phenylacetic acid; 3) myelosan, sarcolysine, spirazidine; 4) antioxidant; 5) nitrosomethylurea; 6) 6-mercaptopurine; 7) 5-fluorouracil; 8) adrenaline; 9) irradiation with a dose of 450 r; 10) cold; the horizontal dashed line indicates the normal value of AOA; t_r = the recommended instant for repeated administration[240].

An inverse correlation between antitumour activity and $(AOA)_{min}$—the minimum value of AOA which can be attained by a given antitumour treatment (Fig.40)—has been established for the model of the transplantable leukaemia La. On the basis of this correlation, it is possible to develop a new principle of the screening of antitumour preparations in which healthy animals are used to determine their effectiveness.

The study of the antioxidant properties of tissues can be used also for a rational selection of preparations with anticarcinogenic properties. The changes in the AOA of tissues in carcinogenesis correspond to the morphological stages of the latter (Fig.41).[271] It has been shown that, in the stage involving a decrease of AOA, anticarcinogenic activity is shown by preparations which increase AOA to values close to the norm; at later stages of carcinogenesis it is necessary to decrease AOA.[271,272] Thus at a given stage of carcinogenesis the AOA test makes it possible to establish the dose in which the antioxidant will exhibit an effect retarding carcinogenesis.

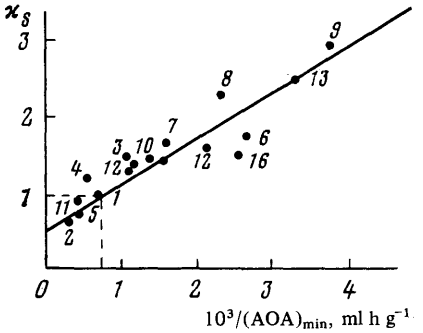


Figure 40. Dependence of the inhibition coefficient $\varkappa_S$ for transplanted leukaemia La on the reciprocal of the minimum AOA of lipids under the influence of antitumour preparations and other types of treatment[268].

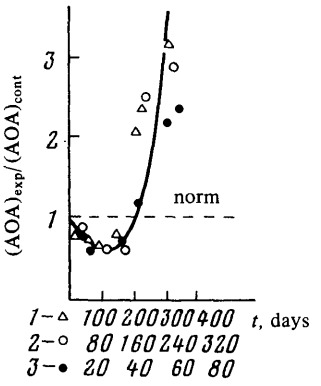


Figure 41. Variation of the AOA of mouse liver lipids in carcinogenesis; 1) o-aminoazotoluene; 2) γ-radiation; 3) 3,4-benzpyrene.[268]

9. Kinetic Aspects of the Ageing of Living Organisms. Physicochemical Principles of Increasing the Life Span

The ageing of man is one of the most dramatic laws of nature. A wide variety of processes in the living organism take place in open heterophase chemical systems under the influence of numerous chemical and physical factors. Many of the undesirable and "harmful" phenomena in chemistry are

also referred to as ageing processes. These are, for example, the ageing processes in polymers and articles made from them, examined above, the spoiling of food products and medicinal preparations, etc. Many processes with analogous elementary process mechanisms (molecular, ionic, and free-radical) take place both in the ageing of "non-living" chemical systems and in the ageing of living organisms. The entire experience concerning the control of chemical reactions gained in the study of chemical kinetics should be reasonably employed for the inhibition and suppression of ageing processes in living organisms.

There is as yet no single accepted method for the measurement of the rates of ageing of individual organisms in gerontology, although various procedures have been proposed for the determination of "biological age". Instead, statistical ageing indices, referring to a group of similar individuals, are usually employed. The main effect of ageing is that the probability of death in the forthcoming period of time (year, month, etc.) increases with age. The principal statistical ageing indices are therefore derivable from the survival curve. The survival curve $P(t)$ represents a function describing the dependence of the fraction of surviving organisms P on their age t. The principal mortality indices such as the mortality rate dP/dt and the quantity $R_m = (1/P) \cdot (dP/dt)$, which has come to be referred to as the strength, intensity, or index of mortality, can be derived from the survival curve. In the absence of ageing $R_m = \text{const.}$, i.e. is independent of the age; ageing processes are manifested by the fact that R_m increases with age. The survival curve also yields other indices, such as the average and maximum lifespans, the average remaining lifespan, etc.[239]

Survival curves have the usual complex S-shape. For humans and certain laboratory animals, they can be fitted, for example, by the empirical Gompertz–Makeham formula:

$$R_m = A + R_0 e^{\alpha t}, \qquad (123)$$

where A, R_0, and α are constant parameters. Other empirical formulae are also used for laboratory animals.

The application of the probit method[273] in the treatment of these data makes it possible to represent the survival curve by a straight line making an intercept on the time axis equal to the age of the animals corresponding to 50% mortality ("median"); the average rate of mortality as a percentage can be determined from the slope of the straight line[274]. This method of representing data is particularly clear in those cases where the rate of the ageing process is altered by means of some kind of influence in the course of the experiment, as will be shown below (see also Fig.43).

In the case of effective influences leading to an increase of the lifespan of animals and to a change of particular parameters, the survival curves for the experimental group can differ in shape from the curves from the control group. The group of animals used to determine the survival curve can be divided to a first approximation into two subgroups: "short-lived" and "long-lived". Geroprotectors can have different effects on these subgroups and the nature of the changes in the overall survival curves is accordingly also different[275].

I. If the lifespan of all the members of the group increases by the same amount, the average and maximum lifespans also increase and the survival curve shifts to the right parallel to itself (Fig.42*a*). The mortality rate may not then change.

II. The influence may decrease the mortality rate in the group of "long-lived individuals". In this case the average and maximum lifespans also increase and the survival curve has the form shown in Fig.42*b*.

III. If the lifespan of the subgroup of short-lived individuals increases and the maximum lifespan remains unaltered, the curves have the form shown in Fig.42*c*. The mortality rate then increases but the average lifespan nevertheless also increases.

The proposed subdivision of the experimental group into two subgroups can serve as a basis for the classification of effective influences increasing the lifespan of animals.

Numerous data indicating the involvement of free radicals in ageing processes suggested that inhibitor-antioxidants should exhibit a prophylactic and therapeutic effect and should increase the lifespan of organisms. By preventing the development of different kinds of pathological processes, antioxidants can reduce the amount of damage in organisms and hence can prevent ageing.

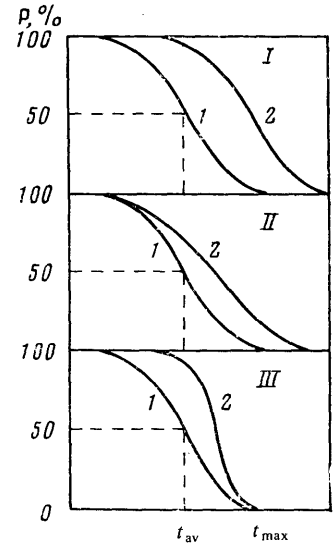
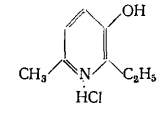


Figure 42. Various types of changes in the survival curve observed experimentally when the organism is treated with agents decreasing the rate of ageing: 1) control; 2) treatment with geroprotector[275].

Harman[276] observed that the addition to food of ionol (2,6-di-t-butyl-4-methylphenol), a well known radical process inhibitor, increases the lifespans of mice on average by 40%. 2-Mercaptoethanolamine, butylhydroxyanisole, and cysteine cause a somewhat smaller increase, the result depending on the breed of the animals. It has been shown[277] that the introduction of the antioxidant santoquin into food also increases the lifespan of mice. The lifespan of animals does not then exceed the maximum known for mice of the given strain under optimum conditions.

The lifespan of laboratory animals is also increased by the relatively non-toxic water-soluble antioxidant 2-ethyl-3-hydroxy-6-methylpyridine hydrochloride, a structural analogue of vitamin B_6:[278–280]



SHK and C3HA mice were given the geroprotector starting from the age of two months. In experiments with two month old SHK animals (Fig.43*a*) an increase of the latent period on the survival curve (the time of attainment of 10% mortality)

and an increase of the maximum lifespan from 25.4 months in the control to 29 months under the influence of the geroprotector were observed. The entire survival curve then underwent a parallel shift to the right. The average lifespan increased to 17.8 ± 6 months compared with 13.7 ± 0.5 months in the control. As a result of the probit transformation for the control and experimental groups, parallel straight lines were obtained. The mortality rate determined from them was 6.2% month^{-1}.

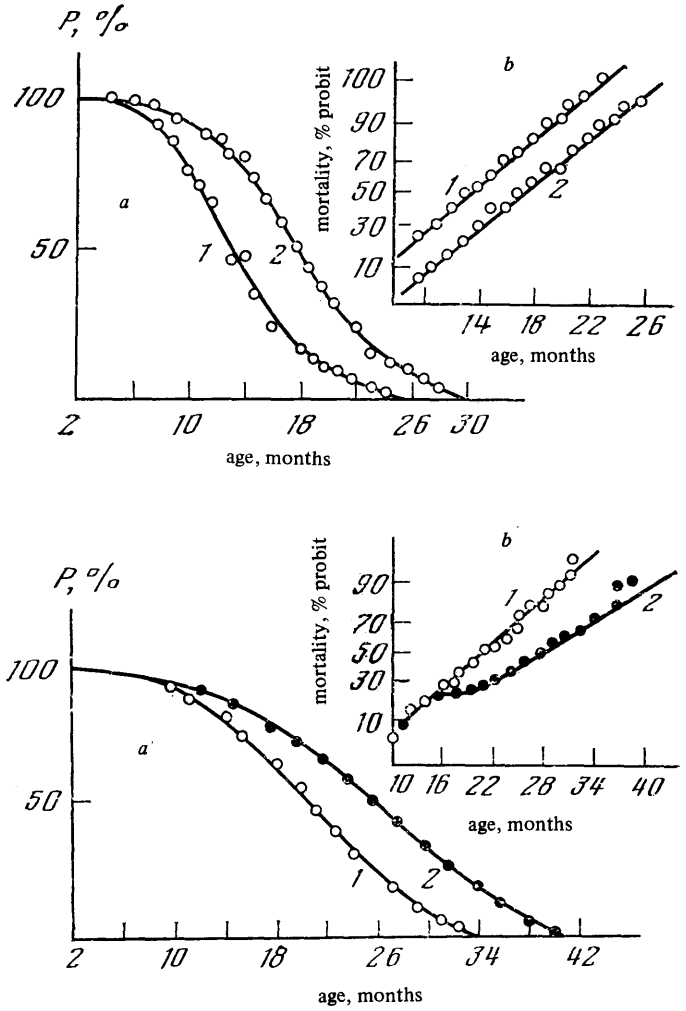


Figure 43. The influence of 2-ethyl-8-hydroxy-6-methylpyridine on the lifespan of SHK (*A*) and C3HA (*B*) mice. Treatment begun at the age of 2 months: *a*) survival curves; *b*) probit transformation; 1) and 2) control and experimental groups respectively[279,280].

Other results were obtained for two month old mice of the C3HA strain (Fig.43*b*). The average experimental lifespan reaches 27.05 ± 0.80 months and the maximum lifespan is 41.2 months compared with 21.90 ± 0.75 and 32 months respectively in the control. Line 2, observed by the probit transformation, has a break in the region of 16 months. The mortality rate decreases to 3.7% month^{-1} compared with 4.7% month^{-1} for the control group.

Comparison of the experimental data with the above analysis of the form of survival curves (Fig.42) shows that the nature of the action of 2-ethyl-3-hydroxy-6-methylpyridine hydrochloride depends on the strain of the animals. The effect of the geroprotector in experiments with two month old SHK mice can be assigned to type 1, since it exerts the same influence on all members of the population. In the case of 2 month old mice of the C3HA strain an effect of type 2 is observed, whereupon the mortality rate of the long-lived section of the population diminishes.

The influence of 2-ethyl-3-hydroxy-6-methylpyridine hydrochloride on the ageing of the Drosophila fly has also been observed reliably. The effectiveness of the geroprotector depends on its concentration, the stage of development of the Drosophila, and the age of the flies at the beginning of the experiment[281].

Experiments on the application of the geroprotector in the larval stage only are of particular interest. It was found that an increase of the lifespan of the adult fly is then observed. It has been suggested that defects leading subsequently to ageing accumulate in the tissues of the larva from which the organs of the adult fly are produced (the nervous tissue and the imaginal buds). The rate of ageing of adult individuals can be retarded by decreasing with the aid of the geroprotector the rate of accumulation of these defects during the larval period. It may be that the DNA molecules retain a "memory" of the geroprotecting effect.

The data obtained show that the kinetic approaches to the study of ageing are promising and that wide possibilities arise in gerontology from the application of antioxidants as geroprotectors.

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This review has dealt with only a few examples of successful application of the methods and ideas of chemical kinetics to various branches of chemistry and biology. There is no doubt that chemical kinetics will make an increasing contribution to the solution of theoretical and practical problems of modern chemistry, chemical engineering, biology, and medicine.

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Transformations of Condensed Substances under Shock-wave Compression in Controlled Thermodynamic Conditions

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The development of dynamic methods of acting on matter is reviewed, with special emphasis on isentropic shock-wave compression methods, which minimise the thermal contribution to the pressure. The effect of pressure, temperature, micro- and macro-plastic deformations, and of pressure relief waves is discussed. Problems arising in studies of the low-temperature compression of condensed gases under dynamic conditions and of chemical synthesis by shock-wave compression of solid-gas systems are examined. 53 references.

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I. INTRODUCTION

The aim of this paper is to examine the possibility of exploiting various regions of the p,T phase diagram of substances (where p is the pressure and T is temperature) and of obtaining high levels of compression under different heating regimes in dynamic experiments. Dynamic interactions include various types of compressive load: from compression by a single or a multiple shock wave (SW) to dynamic isentropic (or, more exactly, nearly isentropic) compression (DIC). Shock waves are generated in condensed substances under dynamic conditions by the detonation of an explosive substance (ES) in contact with the sample, or by impact from a body accelerated to a high velocity by the products of an explosion.

The dynamic approach to the physics and chemistry of high pressures includes: a) studies of the state of substances during shock-wave compression (measurement of the compressibility and construction of the equations of state, study of the visco-elastic characteristics and of the optical and electrical properties, study of the low-temperature plasma generated by the pressure relief following a shock wave in a porous substance), and b) studies of the physicochemical transformations of substances contained in strong vessels (sample preservation bulbs) after shock-wave compression. The latter approach has attracted a great deal of interest during the past two decades because of the possibility of its direct practical application in synthetic work under SW conditions.

Some aspects of high-pressure physics and chemistry are related to the physics of high energy densities.

A generalised p,T diagram (Fig.1*a*) shows (as cross-hatched areas) the regions of high static or dynamic pressure which have so far been exploited. In order to simplify the diagram the regions of ~10^3 GPa and 10^4–10^5 K (explored in compression experiments[1]) and of a few hundred GPa at 10^3–10^4 K (in experiments with preservation of the sample[2]), mainly involving an axially symmetrical loading geometry, have not been included.

The static method has one undeniable advantage: it allows the sample to be exposed to high pressures and temperatures for long times, and therefore the two parameters can be varied in the desired sequence (Fig.1*b*). The initial substance is usually first compressed, then heated, and at the end of the experiment the temperature is lowered before the pressure. This allows metastable states to be preserved under normal conditions. A general review of the thermodynamics and kinetics of reactions under static compression conditions is given in Ref.3.

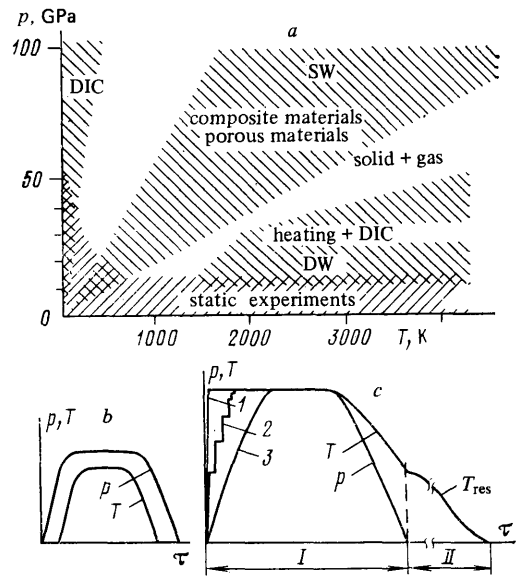


Figure 1. Generalised p,T diagram showing the regions of high static or dynamic pressure application (*a*), and idealised plots of p and T against time under static (*b*) and under dynamic conditions (*c*); DIC is the dynamic isentropic compression region, SW is the region of shock-wave compression of composite or porous solid materials, and of gas–solid systems, DW is the region of high p and T values generated in a detonation wave; *1*), *2*), and *3*) are the wave fronts for single and for multiple shock compression, and for DIC, respectively. Cooling rate ~10^8 K s^{-1}; the durations of processes I and II are ~10^{-5} s and ~1 s respectively.

Shock compression does not offer these advantages. Both the pressure and the temperature rise in a narrow zone (the SW front) in times of 10^{-12}–10^{-9} s, after which the pressure relaxes in ~10^{-6} s through isentropic pressure relief waves, while the temperature falls to some intermediate value (T_{res}, see Fig.1c) owing to the irreversibility of the shock compression. The whole process is completed in ~10^{-5} s: the final cooling of the depressurised sample follows the normal heat conduction laws. Obviously, high-pressure phases can be eliminated by high residual temperatures unless special precautions are taken (e.g., the back-graphitisation of the diamond formed by shock-wave compression).

Nevertheless, the shock interaction method has a number of specific features and advantages, including the ease with which ultra-high pressures and temperatures can be achieved, the generation of extremely high shear strains on the SW front (which give anomalously high rates of physicochemical reactions in the solid state), extremely fast cooling rates, strict control of the development of pressure, etc. All these advantages have been exploited in studies of physical and chemical changes in experiments with preservation of the sample, and shock compression has been shown to lead to defect formation, complex chemical reactions, polymorphism, etc.

This review will deal with the basic problems in the development of the SW method, and with the results obtained in diagnostic experiments on the factors (temperature, pressure, microscopic or macroscopic plastic deformation, pressure relief waves) responsible for various processes. The problem of achieving low-temperature compression under dynamic conditions will be examined in detail.

II. THE SHOCK-WAVE COMPRESSION REGION

Most of the work on the dynamic aspects of high-pressure physics and chemistry so far reported refers to the SW region (Fig.1a). Studies of the properties of matter under the influence of shock compression have been discussed in many monographs and reviews (see, for example, Refs.4–12). Studies of the properties retained after compression have shown[13–16] that the very short duration of the shock compression process is not a serious obstacle to the widespread use of the method. The products can be preserved after relief of the pressure if the residual temperature is not too high (a condition easily satisfied by the enormous cooling rates (~10^8 K s^{-1}) accompanying the decrease in pressure). However, many processes can take place as a post-effect, i.e. after relief of the pressure, if the residual temperature of the material activated by the SW front is relatively high. This unique situation is never encountered except in SW systems.

1. Planar Loading Scheme

SW application from one side only in the planar variant (Fig.2a) allows the development of pressure to be calculated with high precision. Macro-plastic deformation of samples in bulbs, mainly during pressure relief, is usually less than 10% at moderately high pressures. Low-density substances can easily be compressed to 50 GPa by repeated SW, reflected from the denser metallic walls of the bulb. By using a flat bulb design the samples can be pre-cooled to 4.2 K: a very important facility for studies of thermally unstable states[17]. The retention of these states is assisted by fast heat transfer from the experimental region towards the bulb walls at the end of the shock compression process. Even more marked effects are obtained by rapidly cooling the bulb at the end of the experiment (for example, to 77 K [17]).

Systematic comparative studies of organic reactions initiated by SW (in particular, the shock polymerisation of acrylamide[18]) have revealed a strong dependence of the final state of the sample on the initial temperature (T_0). At T_0 = 77 K the reaction products are found (by ESR) to include a fairly high concentration of paramagnetic active centres (AC): 10^{20}–10^{21} kg^{-1}. Furthermore, the presence of these centres gives rise to post-polymerisation even within the thermal explosion period, but no post-polymerisation is observed for T_0 = 293 K.

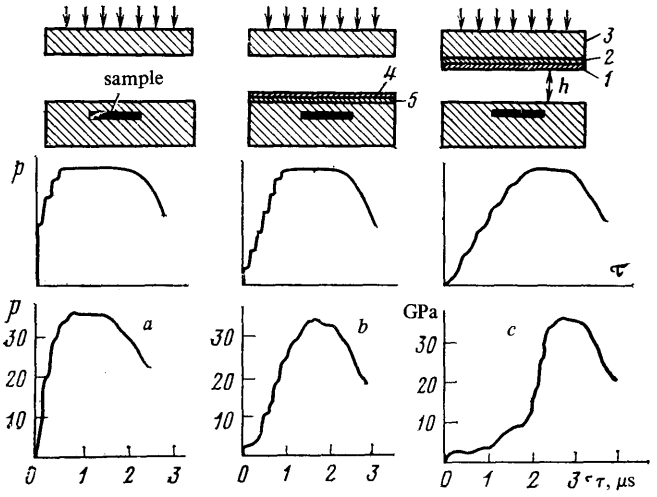


Figure 2. Schematic diagrams of the generation of multiple shock compression (*a*) and of dynamic isentropic compression (*b* and *c*), with idealised and experimental compression wave profiles: *1*), *2*), and *3*) are Perspex, aluminium, and copper plates; 4) and 5) are copper and Perspex plates.

Gamma-irradiation of many monomers at low temperatures is known to lead to the formation of stabilised ACs, which cause polymerisation if the temperature is raised. The combined effect of γ-radiation and SW on acrylamide samples has been studied[19] at 77 K. After pre-irradiation with 5–6 Mrad doses, shock compression was found to increase the yield of polymer to a level higher than the sum of the contributions from the separate agencies. This observation can be ascribed to the transition of the polymerisation process to the thermal explosion regime owing to the high rate of heat evolution produced by the simultaneous radiation-chemical and mechanical initiation of ACs.

We should note that studies of defects in materials exposed to shock compression have shown that the changes in the sample are not equivalent to simple thermal dissociation, and that the final product is often similar to the product of radiation-induced decomposition[14].

A comparative study of the thermal decomposition of ammonium perchlorate samples previously exposed to γ-radiation (1 Mrad dose) or to shock compression (1.5–20 GPa) has been reported[20]. Differential thermal analysis of these samples has shown a substantial decrease in thermal stability in both cases: decomposition begins at 490–500 K, whereas the initial sample of ammonium perchlorate begins to decompose at 563 K. The extent of decomposition in the low-temperature stage of the process increased more than three-fold.

Increasing the amplitude of the SW to 20 GPa causes 96% decomposition of the sample in a single step at 490 K. Thus, irradiation and SW treatment of ammonium perchlorate give very similar results.

We should stress that samples exposed to shock treatment develop defects similar to those found in irradiated samples[14]. In particular, Lisin points out[21] that irradiation of solids by powerful beams can give rise to localised SW, but this hypothesis needs to be confirmed experimentally.

2. Cylindrical Loading Scheme

Bulbs having a cylindrical geometry are most often used in experiments with preservation of the sample after shock compression. The creation of a three-impact configuration in a sample contained in a cylindrical bulb by a glancing detonation wave allowed the pressures to be calculated[2] and thus greatly advanced the development of the physics and chemistry of high dynamic pressures. The proof[2] that the detonation velocity of the explosive surrounding the bulb is equal to the rate of propagation of the three-impact configuration justifies the calculation of pressure in the sample without special direct measurements (if the shock-wave adiabatic curve of the sample is known).

Under these conditions pressures of several hundred GPa can easily be obtained. Thus, by using explosives having detonation velocities of $\sim 8 \times 10^3$ m s^{-1}, pressures of ~500 GPa have been obtained in monolithic tungsten samples, and ~60 GPa in sodium chloride[2]. The pressure in the salt can be raised to 100 GPa or higher simply by mixing the salt with tungsten powder. By using a low salt content, and by making the sample denser by repeated SW compression, pressures as high as 500 GPa can be obtained, accompanied by very high temperatures (10^3–10^4 K). The compression conditions generated in the cylindrical loading scheme are convenient for chemical syntheses (which are also favoured by the very strong macro-plastic deformations).

3. Shock Compression of the Solid–Gas System

The simplest system of this type is a low-density substance with pores filled with water at atmospheric pressure. If the solid particles are small, shock compression in these systems can be assumed to cause pressure equalisation, but not thermal equilibrium. Because of the small mass of the air its contribution to the temperature is insignificant, and the average temperature of the mixture will not differ substantially from that of the solid component, in spite of the much stronger heating of the air in the micro-pores in the initial stage of compression.

Under powerful shock compression a porous medium experiences a strong deformation than a continuous medium, and as a result its entropy increases by a greater amount than that of the continuous medium compressed to the same final pressure[7] (Fig. 1*a*). Shock compression under vacuum can produce temperatures of tens of thousands of degrees, and convert part of the sample into the plasma state[23]: this can give rise to thermionic electron emission[24].

Shock compression of porous substances does not cause special difficulties in the preservation of the compression products. Complications arise only if the sample decomposes, or reacts with the large volume of gas evolved, or if the pores are previously filled with gases compressed to high pressures or condensed. Under these conditions the bulbs usually burst as a result of the high internal pressures developed. A special bulb design is needed to prevent bursting. Obviously, partial (or complete) reaction of the evolved gas to form a solid helps the preservation of the sample.

We have recently carried out a systematic study of the design of sample preservation bulbs of the planar and of the cylindrical type for the shock compression of solid–gas mixtures in various chemical investigations[25,26], and we have developed a bulb for the planar loading (up to 40 GPa) of porous substances mixed with gases for initial temperatures of $T_0 \cong 300$ and 77 K.[25] The gas (for example, hydrogen) is admitted under pressure to the working volume of the bulb through a thin connecting tube from a standard or a special gas storage cylinder. These bulbs are not fractured by the shock compression of their contents, and the solid products of the transformation can be examined. On the other hand the excess of gas is lost through the open vent provided.

Cylindrical bulbs offer an extended pressure range and substantial macroplastic deformations, with their associated heating effects, which assist chemical reactions. This feature allows the required gas to be produced during the experiment by compression of a "donor" of this gas (for example, a source of oxygen) either mixed with the sample or separately located[26]. As in the planar variant, the design of these bulbs allows the addition of gases from cylinders as well as cooling of the sample to 77 K. With a solid sample having a high dynamic stiffness the pressure in the mixture can reach 100 GPa or more. Unlike the planar variant, however, this variant allows the bulb to remain sealed during the compression, giving a product at some intermediate (residual) pressure.

We have used these bulbs to study the interaction of various substances with nitrogen, solid carbon dioxide, oxygen, and hydrogen. In particular, we have demonstrated the formation of niobium nitride and carbide by shock-wave compression of a mixture of niobium powder and liquid nitrogen or carbon dioxide[25]. In an attempt to prepare solid CO_2 under normal conditions we have studied[26] the oxidation of SiC under shock compression of a bulb containing a mixture of powdered SiC and gaseous or liquid oxygen. The products were examined by X-ray diffraction and i.r. spectroscopy, and oxidation of the SiC with formation of a non-molecular lattice structure was detected. Heating the oxidised SiC to 800–1300 K produces oxides of carbon.

The interaction of various metals with hydrogen yielded hydrogen compounds of titanium, manganese, and other substances. Saturated hydrocarbons, or water, can be used as hydrogen sources in these reactions.

III. METHODS OF CONTROLLING THE THERMODYNAMIC PARAMETERS DURING DYNAMIC COMPRESSION

Because pressure and temperature in the SW front are closely interrelated, the scope for achieving high pressures without a correspondingly high level of heating is very limited (DIC region in Fig. 1*a*). The possibility in principle of minimising the self-heating of the sample during shock compression by a stepped application of the pressure has been exploited, for example, in measurements of the compressibility as well as in experiments with preservation of the sample. Various experimental schemes for sample preservation under industrial conditions can be used to apply either single or multiple shock loading with variable final pressures, initial temperatures, etc.

By using multiple shock compression the entropy can be decreased very substantially (as compared with one-step compression to the same final pressure). However, in the multiple SW compression of very compressible condensed substances the amplitude of the first SW has to be very high in order to reach a high pressure, and its contribution to the

final temperature rise is predominant. For example, in the multiple shock compression of Perspex to pressures of 50 and 100 GPa the amplitude of the first SW must be ~10 and 20 GPa respectively, corresponding to maximum temperatures of 770 and 1570 K and residual temperatures of 520 and 860 K respectively[9].

Obviously, in order to achieve low-temperature dynamic compression we must lower the amplitude of the first SW and increase the number of compressions. In our work these requirements were met by using layer systems[27]. Clearly, a "smooth" dynamic compression could be achieved also by other methods: some of these are described in Refs. 28–30. However, magnetic accumulation generators[30] seem hardly likely to be compatible with experiments requiring preservation of the sample.

1. Layer Systems

The simplest experimental schemes for the planar leading variant (though they are applicable in principle to axially symmetrical loading) are shown in Fig. 2 for: (*a*) multiple shock compression, (*b*) compression by a SW transmitted through a system of screens having different dynamic stiffnesses, and (*c*) compression by successive impacts from an assembly of striker plates made from high dynamic stiffness materials moving towards the target at different times. By using the layer system in scheme (*b*) it has been possible[31] to lower the amplitude of the first SW to 3 GPa while achieving multiple shock compression to 50 GPa of organic substances having densities of ~10^3 kg m^{-3}.

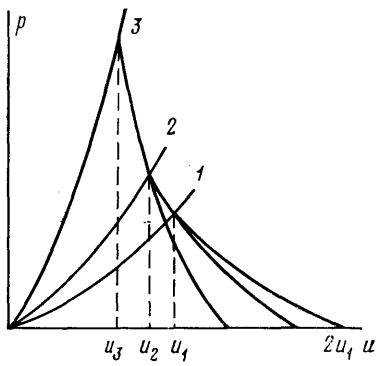


Figure 3. Shock compression adiabatic curves for Perspex (*1*), aluminium (*2*), and copper (*3*), and pressure relief adiabatic curves for the same materials plotted as pressure against mass velocity.

Loading by scheme (*c*) produces a complicated compression pattern, due to the possibility of interaction between the strikers after reflection from the target, spallation phenomena, etc.[32] Therefore it is advisable to plot the true loading profiles produced by the compression waves (using Manganin pressure sensors[27]). The principle of operation of scheme (*c*) is illustrated in Fig. 3. The planar detonation of the explosive charge sends a shock wave through the system of striker plates (e.g. copper, aluminium, and Perspex) whose shock-wave adiabatic curves are shown in the Figure in *p*,*u* coordinates (where *u* is the mass velocity of the material behind the SW front). When the shock wave reaches the free surface the Perspex plate is accelerated to a velocity approximately double the mass velocity of Perspex (since the velocity upon removal of the load is equal to the mass velocity); the aluminium (and especially the copper) striker will have lower speeds. Load is applied to the target containing the sample by successive impacts from the striker plates, the final pressure being determined by the impact of the copper plate (of thickness greater than the combined thicknesses of the aluminium and the Perspex plate).

A qualitative analysis of this method suggests that by varying the relative dynamic stiffness of the plate materials, their thickness, and the distance from the layered striker to the target (*h*), it should be possible to produce compression waves with different profiles: from a pressure increasing monotonically with time to a "saw-tooth" profile with gradually increasing pressure plates. The method allows the time of application of the pressure to be increased to 10 μs or more in large-scale applications. If the damping law which applies to the collision of the first (thin) striker in the target is known, the geometry of the experiment can be designed so as to make the amplitude of the SW reaching the sample during the first compression step negligibly small.

Because of their low thermal stability, organic substances can be used as "thermal indicators" in the search for suitable low-temperature compression conditions. Large differences in the final state of the sample were noted in comparative experiments on the dynamic compression of organic compounds with sample preservation by the schemes of Fig. 2*a*, *b*, and *c* with constant (50 GPa) final pressure and initial (room) temperature. Whereas conventional multiple SW compression of acrylamide caused full thermal degradation of the sample, compression by schemes (*b*) and (*c*) did not degrade the material, nor was degradation observed during the structural transformation in polypropylene. On the other hand compression by scheme (*a*) to 20 GPa or above converts any propylene structure into a microspherulitic phase, because the polymer activated by the SW front is exposed to a relatively high residual temperature.

These results suggest the possibility of achieving a substantially isentropic condition in dynamic experiments.

2. Dynamic Isentropic Compression of Condensed Substances at Low Initial Temperatures

The solution of many problems such as metallisation of dielectrics (including compressed gases) requires high degrees of compression, as well as low temperatures in the case of compressed gases. For a given compression, the temperature on the isentrope is proportional to the initial temperature of the samples. Hence, in order to achieve the lowest possible temperatures in dynamic experiments the interaction with isentropic compression waves is carried out after pre-cooling the sample to temperatures as low as 4.2 K.

We shall discuss below the results obtained for multiple shock compression and DIC of acrylamide samples in copper bulbs at pressures up to 40 GPa and initial temperatures of 10, 77, and 293 K.[17] After the experiments the bulbs were cooled back to 77 K in order to determine the relative amount of products formed.

The compression conditions of samples loaded in different ways can be determined, and their temperatures estimated, by using data on the compressibility of Perspex, whose density is similar to that of acrylamide and which has been fully investigated at high pressures. Under the multiple collision compression conditions used in Ref. 17 most of the

heat is generated by the first SW, which has an amplitude of ~8 GPa, and the subsequent compression waves (up to 40 GPa) can be treated as isentropic. The Grüneisen coefficient was assumed to depend on volume only, and the specific heat on temperature[33]. The calculated results (Table 1) show that the heating effect under DIC conditions is much weaker (especially for $T_0 = 10$ K) than under shock compression. It is also clear that under shock compression the residual temperature effect is substantially lowered for $T_0 < 77$ K, and the residual temperature of the bulb wall can be made even lower with $T_0 = 10$ K.

Table 1. Sample temperatures (K) calculated for different compression conditions ($p = 40$ GPa).

T_0	T_{DIC}	T_{SW}	T_{res}	T^*_{res}
10	24	545	320	30
77	124	565	330	90
293	480	765	445	310

*Residual temperature of the bulb.

These experiments revealed large differences in the yield of polymer from acrylamide and in the rate of the polymerisation process. Shock compression at $T_0 = 10$ K gives 10% of acrylamide polymer during the compression or within a few seconds. The concentration of growing polymer chains is high, and thawing the sample to 293 K results in strong polymerisation with a final yield of 40%. Evidently, the rapid removal of heat from the sample towards the bulb wall (Table 1) helps to retain the ACs. At 77 K the yield of polymer is 30%, and post-polymerisation does not take place on thawing the sample because the ACs are lost by annealing at the relatively high residual temperatures. Shock compression of acrylamide at $T_0 = 293$ K causes only thermal decomposition of the sample.

Under DIC conditions and $T_0 = 10$ or 77 K the yield of polymer does not exceed 2–3%, and no polymerisation takes place on thawing the sample, because of the small number of ACs resulting from the relatively modest pressure gradients at the SW front; DIC at $T_0 = 293$ K gives a higher yield of polymer (20%), but no thermal degradation is observed. From the above comparison of SW compression and DIC we may conclude that polymerisation under shock compression is initiated by the SW front.

Studies of the low-temperature compression of gases and of gas systems were stimulated by the growing interest in the transition of hydrogen to the metallic state. Clearly, the only suitable experimental region in this case was the DIC region (Fig. 1*a*). As we have already pointed out, the procedure used in our experiments for realising these conditions in practice relied on the use of conventional explosives. Most of the work was carried out with gases and gas systems frozen at 77 K. Special bulbs were designed to preserve the samples after dynamic compression to 50 GPa. Immediately after the experiment the bulb with its charge were cooled back to 77 K, opened at that temperature, and the physicochemical properties of the products were studied at and above 77 K.

Carbon dioxide, chlorine, water, a mixture of water and carbon dioxide, and a mixture of n-heptane and chlorine were also investigated. Changes in state of these substances at low temperatures were monitored by the radiothermoluminescence (RTL) method[34]. Compression was found to affect the RTL spectra of many substances. For example, new peaks appear in the glow-curve of CO_2 after compression. After DIC, a mixture of C_7H_{16} and Cl_2 can no longer react rapidly at 153 K, unlike the initial mixture. Other similar results were also reported.

The most important outcome of this type of experiment so far has been the demonstration of the possibility of working with condensed gases under dynamic compression with preservation of the products and direct observation of their properties.

3. Dynamic Isentropic Compression of Condensed Substances at High Initial Temperatures

The main difference between shock compression and DIC lies in the leading edge of the compression wave (Fig. 4*a* and 4*b*). In the case of DIC the microscopic shear deformations and the excess temperatures at the front are smaller even than in multiple shock compression. On the other hand the time of exposure to high pressures, the rate at which the pressure relaxes, and the amount of macroscopic plastic deformation of the bulb and sample after relief of the pressure are practically the same for shock compression and for DIC.

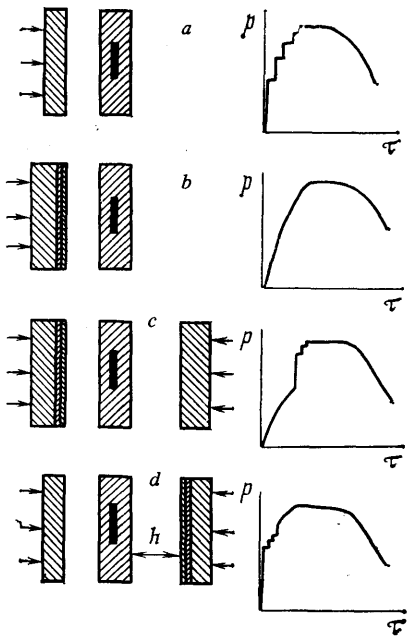


Figure 4. Main loading schemes and idealised profiles of the compression wave: (*a*) multiple shock compression, (*b*) dynamic isentropic compression, (*c*) combination of DIC and shock compression, (*d*) combination of shock compression and DIC.

As has already been stated, DIC of acrylamide samples at $T_0 = 293$ K does not cause thermal degradation: the concentration of ACs is small, and no post-polymerisation is observed. These observations suggest that the SW front is

responsible for the initiation and development of polymerisation during shock compression. However, the DIC experiment alone cannot distinguish the relative roles of micro-shear deformation and of the temperature factor, since any decrease in the effect of the former is invariably accompanied by a decrease in the temperature of the substance at the compression front. Preliminary heating of the sample under DIC conditions should yield p,T conditions identical to those of the conventional multiple shock compression arrangement, but without substantial micro-shear deformations, thus revealing the effect of the SW front in a "pure" form.

With that aim, we have studied the effect of pre-heating in conjunction with DIC on two quite different processes under shock compression: the chemical polymerisation and the structural transformation of graphitic boron nitride (g-BN) into the dense, wurtzite-like modification (w-BN).[35]

The main experimental arrangements and the corresponding idealised pressure profiles are shown in Fig.4*a* and 4*b*. Planar multiple shock compression at pressures up to 20 GPa of samples 2×10^{-3} m thick contained in a bulb was applied by impact from a copper plate 7×10^{-3} m thick; DIC to approximately the same pressure (Fig.4*b*) was achieved by layered Perspex, aluminium, and copper strikers 1×10^{-3}, 2×10^{-3}, and 7×10^{-3} m thick respectively. A more detailed description of the experimental arrangements is given in Ref.35.

Table 2. Yield of polymer (W), concentration of polymer chains (N), and increase in the final and in the residual temperature (ΔT (K) $= T - T_0$) under shock compression and DIC conditions for high initial temperatures.

T_0, K	W, %	$10^{-20}N$, kg^{-1}	ΔT_{fin}	ΔT_{res}
293	30	SW 4.7	220	120
293	2	DIC 1.7	75	0
323	7.5	1.7	135	0
348	13	1.7	170	0

Polymerisation of acrylamide. The polymerisation process requires both the presence of ACs and heating, since activation energy must be supplied to allow the chains to grow. Under shock compression the SW front satisfies both these requirements. As Table 2 shows, shock compression of acrylamide at 293 K gives the polymer in 30% yield. The concentration of polymer chains under these conditions is 4.7×10^{20} kg^{-1}. The yield of polymer under DIC conditions at 293 K is an order of magnitude less, with a concentration of polymer chains three times smaller and unaffected by an increase in the initial temperature almost to the melting point of the monomer. The increase in the yield of polymer (to 13%) is due to the higher residual temperature.

Since the pressure and the residual temperature for shock compression at $T_0 = 293$ K and for DIC at $T_0 = 323$ K are not very different (according to calculations of the residual temperature similar to those used in Table 1), the formation of a greater number of polymer chains under shock compression conditions suggests that the SW front plays a dominant role in the generation of ACs and in bringing about the polymerisation reaction during shock compression. In the present example the concentration of Acs was 10^{20} kg^{-1}, and their time of formation was 10^{-6} s or less, corresponding to the strikingly high rate of generation of 10^{26} kg^{-1} s^{-1}.

g-BN–w-BN *transformation.* Shock compression of graphitic boron nitride to pressures higher than 12 GPa is known to cause irreversible transformation into a dense wurtzite-like modification. Two explanations have been put forward to account for the high speed of this transformation[36,37]: 1) strong shear deformations and 2) a martensitic type of transformation, proceeding athermally and under the influence of pressure alone.

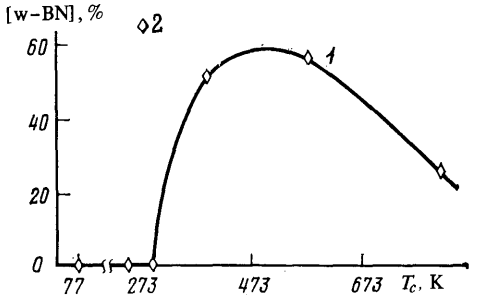


Figure 5. Yield of dense boron nitride phase against initial temperature: *1*) dynamic isentropic compression, *2*) shock compression.

By exploiting the application of almost isentropic compression in dynamic experiments at different initial temperatures we can distinguish between these alternative explanations. The results show (Fig.5) that if multiple shock compression is replaced by DIC at low or at normal temperatures the phase transformation in boron nitride is inhibited. However, a preliminary heating of the sample is sufficient to restore the transformation, even under conditions close to isentropic compression. Stronger pre-heating of the sample causes partial annealing of the dense boron nitride phase after removal of the pressure.

These results suggest[35] that a simple increase in pressure is insufficient to cause the g-BN–w-BN transformation in times of $\sim 10^{-5}$–10^{-6} s. An increase of temperature is also required in order to overcome the substantial activational barrier.

About 20 years ago, when structural transformations by shock compression were first reported[52,53], the possibility of SW generation in the deeper layers of the Earth by the sudden movement of rock formations was considered in relation to the generation of dense phases and to the initiation of earthquakes. Of course, these conditions are possible, but the generation and more sustained existence of strong and smooth pressure waves seems more likely (for example, after the passage of a SW). Because of the uneven temperature distribution in the Earth's core (varying by hundreds of degrees over distances of 100 km), and noting the above experimental results, we can expect transformations over large volumes in the depth of the Earth not only in regions which can support shock waves but also at greater depths, where the SW is transformed into a smooth compression wave.

Bridgman[38] recently suggested that SW pressure could be applied to a sample already under static compression. Our simple method of generating almost isentropic compression in dynamic experiments can be used to produce conditions in which a sample which has been compressed "smoothly" and with negligible heating (especially at low initial temperatures)

is subsequently subjected to shock compression (Fig. 4*c*). The opposite situation can also be arranged: isentropic compression of a shock-compressed sample (Fig. 4*d*).

Modern explosive handling techniques allow very precise synchronisation of the detonation of the charges used for launching the strikers. The required distance from the striker to the target (shown as *h* in Fig. 4*d*) and the corresponding pressure can be calculated from the *p*,*u* diagram if the shock-wave adiabatic curves of the materials and the striker velocities are known. For small sample thicknesses the pressure due to the reflected SW is equal to the pressure in the bulb material.

Frontal collision of compression waves has been used so far only in studies of compressibility and electrical conductivity by shock compression[39,49]. The above discussion shows that both shock waves and isentropic compression waves can be used (in their various combinations) to generate frontal collisions. In other words, we can now apply different types of controlled dynamic loading to a sample, and we can monitor changes in the state of the sample both during its compression and by direct analysis of the preserved sample.

IV. EFFECT OF PRESSURE RELIEF WAVES ON THE PHYSICOCHEMICAL TRANSFORMATIONS OF CONDENSED SUBSTANCES

After shock-wave compression the sample invariably experiences pressure relief waves which have the effect of removing both the pressure and the excess temperature in times of $\sim 10^{-5}$ s. Let us examine the planar loading scheme, which offers a simpler variant of sample compression. In the experiments with sample preservation the sample is located outside the disruptive load region formed by the interaction of opposing pressure relief waves. Therefore the sample is exposed to the pressure relief waves, and its pressure can fall to atmospheric (in most cases). With very short SW, generated by the impact of a thin (2–3 mm thick) plate, the pressure in the sample is relieved by overtaking relief waves from the direction of the free surface of the striker. The extent of macro-plastic deformation for moderate pressures is not very great in this case (1–2%). When the SW is generated by impact from a thick plate, or by the contact detonation of an explosive charge, the residual deformation of the bulb and sample can be as high as 10%.

There are no estimates so far in the published literature of the temperatures produced by deformation, nor is there any evidence on the formation of defects or on structural transformations by the pressure relief waves during the fall of the pressure to atmospheric levels. We shall attempt to answer these questions by using the results of comparative studies of substances subjected to shock-wave and to dynamic isentropic compression respectively, given in sub-section 3 of the previous Section.

Comparison of the two sets of results for acrylamide at 293 K (Table 2) shows that the combined effect of micro-plastic deformations and high temperatures, characteristic of shock compression, increases the yield of polymer by a factor of 10 and the number of ACs (assuming the concentration of polymer chains to be proportional to the concentration of ACs) approximately 3-fold. Hence we may conclude that the number of ACs formed by pressure relief waves and by macro-plastic deformations during shock compression is one-third of the total. The relative proportions of ACs formed by pressure relief and by deformation respectively cannot be estimated at present. Since the character of the pressure relief and the extent of macro-plastic deformation are very similar in SW compression and in DIC it would appear that the contribution of the pressure relief waves to the initiation of polymerisation is negligible in comparison with the contribution of the SW front.

Let us examine a different type of transformation: the formation of dense phases by shock compression. Multiple shock compression of g-BN samples to 20 GPa gives the dense w-BN phase in ~70% yield (Fig. 5). If DIC is used at initial temperatures in the range 77–293 K the dense phase is not formed, in spite of the increased macroplastic deformation produced by the "discharge" of material into the free volume of the bulb.

The conversion of g-BN into the dense phase under shock compression occurs at 12–20 GPa pressures in the presence of high temperatures. If the temperature rise produced by the presssure relief waves and by the resulting macro-plastic deformations in this pressure range were sufficient to bring about the transformation, a dense phase would be detected in the boron nitride samples preserved after DIC. The absence of w-BN is evidence that the macro-plastic deformations have failed to raise the temperature of the g-BN sufficiently. The results obtained for DIC with high initial temperatures (Fig. 5) show that the temperature rise of the sample under these conditions is not very marked.

A third example can be taken from Ref. 41, which describes a metallographic study of copper single crystals and of nickel and brass polycrystals exposed to DIC conditions (changing to shock compression within the sample). The DIC was produced by multiple reflection of SW in an intermediate layer (between the striker plate and the target, see Fig. 2*b*) consisting of a low-density material: liquid hydrogen, which also acted as a coolant. The density of deformations and the micro-hardness were found to be lower in the region affected by the DIC than in the shock compression region.

These examples show that the effect of the pressure relief waves on the formation of defects in the sample is very small. When a planar loading scheme and moderately high pressures are used the macro-plastic deformations generated during pressure relief make a negligible contribution to the final residual temperature rise.

We should also mention a report[42] of phase transformations induced by shock compression and giving less dense structures: these are most probably caused by the expansion stresses arising during load removal. However, the exact stage during pressure relief corresponding to these changes is still not clear: they could take place during the decrease of pressure to atmospheric values, or they could require negative (disjoining) pressures. The results[42] are a good illustration of the wide scope of scientific and practical applications of shock waves.

V. DIRECT APPLICATION OF THE HIGH PRESSURES AND TEMPERATURES DEVELOPED DURING THE DETONATION OF EXPLOSIVES

Detonation is the propagation (at supersonic speed) of an exothermic chemical reaction front through a substance capable of sustaining the reaction without the participation of the surrounding medium. The hydrodynamic theory of detonation treats the detonation wave as a shock front followed by a zone of chemical reaction and a zone in which the reaction products are ejected. The detonation wave is propagated at a constant speed because any loss in energy of the SW is immediately replaced by the energy evolved by the chemical reaction in new regions of the sample. The passage of a detonation wave converts solid or liquid compounds into a mixture of gaseous products (CO_2, CO, H_2O, H_2, N_2, etc.) whose density at the end of the reaction zone is $\sim 2 \times 10^3$ kg m^{-3}.

The size of the stationary zone (a) and the duration of the chemical reaction (τ) in the explosive substance depend on a number of factors, such as the power of the explosive and the density of the charge. For example, if the density of TNT is changed from 1.0×10^3 to 1.6×10^3 kg m^{-3} the parameter a changes from 1.6×10^{-3} to 1.0×10^{-3} m, and τ from 0.5 to 0.2 μs. The pressure at the end of the chemical reaction zone changes from 6.5 to 18 GPa. For Hexogen a change in density from 1.0×10^3 to 1.72×10^3 kg m^{-3} changes the a value from 1.4×10^{-3} to 0.7×10^{-3} m, the τ value from 0.4 to 0.1 μs, and the pressure from 9.5 to 30 GPa. These results were obtained[43] by an electromagnetic method. The temperature of the detonation in condensed explosives is 2000–5000 K (Fig.1, DW region).

Several recent publications have described the direct application of the high pressures and temperatures and of the products of the detonation in physicochemical studies of a sample mixed with the explosive. The products were preserved by carrying out the experiments in strong, sealed containers, able to withstand the pressure of the detonation products.

One of these publications[44] describes the synthesis of silicate crystals from a mixture of oxides; others discuss the interaction of the nitrogen formed during the detonation with metal powders to give aluminium, beryllium, boron, magnesium, and zirconium nitrides[45], and the preparation of boron oxide, nitride, and carbide by the reaction of boron with detonation products[46]. The possibility of inducing structural changes under these conditions has been demonstrated[47]: the density dependence of the detonation velocity of a mixture of TNT and quartz was found to include a break, which was interpreted as a phase formation in the quartz.

In the light of these results it is interesting to examine the state of additives affected by a detonation wave. There have been various attempts at describing the establishment of equilibrium between the particles of an inert additive and the detonation products during the chemical reaction period, i.e. during the equilibration of pressure and temperature[48]. Similar problems were considered in a study[47] of the effect of added aluminium on the parameters of the detonation of TNT, and in a calculation[49] of the parameters of detonation waves in mixtures of explosives and inert substances. The detonation of water-filled explosives has attracted much attention, and the addition of water has been shown to enhance the detonation parameters[50]. The water acts as an internal envelope, and it prevents the dispersal of the detonation products, thus increasing the time available for chemical reactions and leading to a more complete evolution of energy. This effect is observed only in explosives with a negative oxygen balance[51].

Let us examine the state of particles of inorganic additives having a density of $\sim 2 \times 10^3$ kg m^{-3}, i.e. close to that of the detonation products, in terms of published results[48–51] and of known features of the shock compression of condensed substances. Because the densities are so similar, the additive in the front will experience a single shock compression, and it will be heated by the SW compression and by the hot detonation products. Clearly, the state of a mixture of inert particles and dense gases in a detonation wave is determined by the reaction time, and by the physical properties (and size) of the particles. We shall take the average size of the chemical reaction zone to be $a \cong 0.5 \times 10^{-3}$ m, and $\tau \cong 10^{-7}$ s. In this case the size of the inorganic particles which are heated, $l \cong (\lambda\tau)^{1/2}$, is ≤ 0.5 μm (where λ is the thermal diffusivity of the material). Pressure equalisation between the detonation products and the particles of the additive will occur in time $\tau_1 \cong l/D$, where D is the velocity of propagation of the shock wave in the additive ($\sim 5 \times 10^3$ m s^{-1} at 20 GPa). In our case the pressure will be equalised for $\tau_1 < \tau$, i.e. for $l < 0.5$ μm. Thus, if the particle size of the additive is <0.5 μm we can expect temperature and pressure equalisation in a heterogeneous detonation zone.

The presence of high temperatures and pressures, and of chemically active products, in the reaction zone of the detonation should stimulate physicochemical changes in the additives. It is important to note that the cooling rate of the detonation products[43] and of the additive particles (or of the resulting compounds) is as high as during pressure relief after shock compression ($\sim 10^8$ K s^{-1}). The only difference is that after shock compression the sample in a preservation bulb remains in a densified state, whereas in the detonation products the particles fly apart: this helps to quench them and to preserve the compounds or the structural changes produced by the detonation.

We should also note that in a detonation wave the high pressures and temperatures can exist for times significantly longer than in the shock compression process. Some reactions probably occur when the detonation products are being ejected but while their temperature and pressure are still high.

In conclusion we should stress that the detonation parameter region (high temperatures and moderate pressures) is not easily accessible in SW experiments. These parameters can be achieved by DIC of previously heated samples (Fig.1*a*), but this approach does not offer the quenching conditions associated with the ejection of detonation products.

VI. CONCLUSIONS

We have shown that the wide range of methods recently developed for generating dynamic pressures can be applied to substances in the pressure range 10–100 GPa (or more) and the temperature range 4.2–10^4 K, and that the state of the sample after this treatment can be studied. The development of nearly isentropic dynamic compression methods is important, because it has allowed high levels of compression to be achieved by lowering the thermal contribution to the pressure generated by shock compression. By using DIC in conjunction with low initial temperatures it has been possible to work with compressed gases and to preserve the products thus obtained. Colliding pressure waves have been shown to create conditions in which an isentropically compressed sample can be additionally subjected to shock compression.

Comparison of the results obtained by shock compression and by DIC at high initial temperatures has established (by a direct experimental method) the role of the SW front in various processes. The conversion of boron nitride into a dense modification has been shown not to involve the strong microshear deformations generated at the SW front, and to be a thermally activated process. A chemical polymerisation reaction has been studied, and shown to be produced by the SW front.

By comparing shock compression and DIC results for moderately high pressures (using planar loading) we have shown that the pressure relief waves in the region of pressure falling to atmospheric levels do not contribute significantly to the creation of defects or to the final (residual) temperature rise of the sample associated with the macroplastic deformations.

Some very revealing experiments on the shock compression of systems including gaseous components have allowed new chemical syntheses to be performed. It appears that high residual temperatures convert a large proportion of the products (and possibly also some other unstable compounds) into the initial compounds. However, the resulting phases can be quenched by pre-cooling the sample. In principle it should be possible to establish conditions similar to those of

static experiments during the final stages of the shock compression (i.e. to cool the sample under high residual pressure). This requires a strong bulb, which will remain gastight after removal of the pressure. Our calculations suggest that samples can be retained under residual pressures of 1 GPa or more. This problem requires further study, and becomes even more complex when the compression products include gases.

We have shown that the region in the p,T diagram of a condensed substance which is not easily accessible in SW experiments (high temperatures at relatively low pressures) can easily be reached by applying dynamic isentropic compression to a pre-heated sample or by exploiting the high pressures and temperatures developed in a detonation wave.

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Kinetics of the Thermal Decomposition of *N*-Nitro-compounds

F.I.Dubovitskii and B.L.Korsunskii

Results primarily on nitramines are summarised. Analysis of modern views indicates that a non-chain radical mechanism with rupture of the N-NO_2 bond in the rate-determining stage is the most soundly based. Kinetic parameters of the thermal decomposition of *N*-nitro-compounds are systematised. The kinetic role of phase constitution is discussed, and prospects for future research are considered. A list of 108 references is included.

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I. INTRODUCTION

The problem of the thermal stability of nitro-compounds is closely connected with those of the explosives industry. Their molecules contain relatively unstable chemical bonds, which are responsible for their great reactivity (and consequent danger involved in handling them under storage conditions and in technical operations).

For a long time estimates of the thermal stability of nitro-compounds were usually empirical in character, although attempts at a kinetic investigation of their thermal decomposition were made as early as the 1920s.[1,2] However, systematic kinetic studies began only with the founding of the Institute of Chemical Physics of the USSR Academy of Sciences in 1931, and these isolated the problem of the thermal decomposition of nitro-compounds as a separate branch of science having immense practical application. A considerable role in establishing this line of research was played by Roginskii, Apin, and Andreev[3-5]. Results obtained during the first few years were surveyed in Semenov's monograph[6].

The present Review is devoted to the kinetics of the thermal decomposition of *N*-nitro-compounds, which include such well known explosives as hexogen, octogen, tetryl, and dina. Reviews on this topic have not been published hitherto.

II. DECOMPOSITION IN THE GAS PHASE

The thermal decomposition of nitro-compounds comprises very many steps, and for the large majority the detailed mechanism remains obscure. Investigators have hitherto concentrated their efforts on elucidating and describing kinetically the primary rate-determining stages, especially as these mainly govern the thermal stability. The extraordinary complexity of the mechanism of pyrolysis led to early studies being made under relatively simple conditions—in the gas phase—uncomplicated by the surrounding medium, with any contribution by secondary reactions reduced to a minimum. The first attempt at such an investigation was made by Flournoy[7] on dimethylnitramine, after which other dialkylnitramines were examined. The main results can be summarised as follows.

Dialkylnitramines decompose in the gas phase with slight autocatalysis. In this respect they differ from most nitro-compounds of other classes—nitro-ethers, aliphatic and aromatic nitro-compounds—which decompose unimolecularly in the gas phase: i.e. the rate of the process is controlled by a single stage. Homolytic rupture of the N–NO_2 bond must be regarded as the first step in the breakdown of nitramines, since the energy of dissociation of this bond was found to coincide, within the limits of experimental error, with the activation energy of the reaction[8-11]. An important point in connection with the mechanism of the gas-phase thermolysis of nitramines is that analysis of the products from dimethylnitramine showed[7] a high yield (80 mole %) of dimethylnitrosamine. The general mechanism of the gas-phase decomposition of dialkylnitramines can be represented by the equations (for dimethylnitramine as example)

$$(CH_3)_2NNO_2 \rightleftarrows (CH_3)_2N + \dot{N}O_2$$
$$(CH_3)_2NNO_2 + NO_2 \rightarrow NO + \text{Oxidation products}$$
$$(CH_3)_2\dot{N} + NO \rightarrow (CH_3)_2NNO$$
$$(CH_3)_2NNO + NO_2 \rightarrow \text{Oxidation products}$$

A noteworthy feature is the reversibility of the first step, which was proved by the introduction of additives capable of reacting rapidly with nitrogen dioxide (to form inactive products) and thereby removing it from the sphere of reaction. Such additives (e.g. formaldehyde) were found[9,12] to accelerate decomposition, but only to a certain limit: on attainment of a certain concentration of additive (corresponding to complete removal of nitrogen dioxide) the kinetics were unaffected by further addition.

Two important conclusions follow from the reversibility of the first stage in the decomposition of nitramines. Firstly, the relatively low chemical activity of dialkylamino-radicals is confirmed. Secondly, the use as inhibitors of substances capable of reacting readily with oxides of nitrogen, a method widely applied to stabilise nitro-compounds, may produce directly contrary effects on nitramines.

An interesting feature of the above mechanism is the tendency to undergo oxidation by nitrogen dioxide, which is characteristic of nitramines in general. Since other classes of nitro-compounds did not in most cases react so readily with nitrogen dioxide, it may be supposed (although the reactions of nitramines with this compound have never been studied) that the reaction centre in the nitramine molecule is the amino-nitrogen atom, which is attacked by an oxygen atom of the nitrogen dioxide.

Table 1 gives activation parameters for the first stage (rupture of the N–NO_2 bond) in the thermal decomposition of dialkylnitramines. The paucity of experimental results does not permit correlation analysis of the kinetic data. However, Table 1 reveals closely similar activation parameters for the

decomposition of all the compounds. Since the activation energy is equal, within the limits of experimental error, to the energy of dissociation of the $N-NO_2$ bond, it is easy to calculate enthalpies of formation of dialkylamino-radicals from those of the corresponding *N*-nitro-compounds. This gave a value 19.8 kcal mole^{-1} for the enthalpy of formation of the diethylamino-radical[12].

Table 1. Activation parameters for thermal decomposition of dialkylnitramines in the gas phase†.

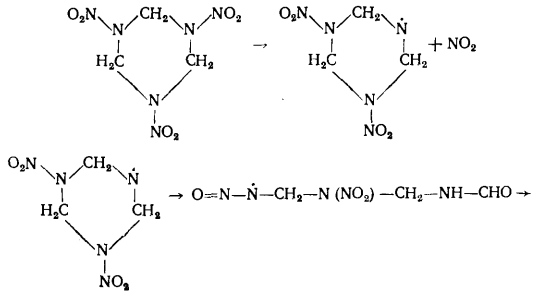
Nitramine	ΔT, °C	E_a, kcal mole^{-1}	A, s^{-1}	Ref.
Dimethylnitramine	180—240	38.9	$10^{13.7}$	[9]
Diethylnitramine	180—240	41.6	$10^{15.1}$	[12]
N-Nitropiperidine	200—240	42.1	$10^{14.8}$	[12]
N-Nitromorpholine	210—245	38.9	$10^{13.6}$	[12]

† ΔT = temperature range of measurements; E_a = activation energy; A = pre-exponential factor.

Several studies have been made of the gas-phase decomposition of the relatively non-volatile cyclic nitramines—hexogen (RDX) (1,3,5-trinitro-1,3,5-triazacyclohexane) and octogen (HMX) (1,3,5,7-tetranitro-1,3,5,7-tetra-azacyclooctane)—whose vapour pressures at temperatures convenient for kinetic measurements are extremely low. Nevertheless, a portion does evaporate when these compounds undergo decomposition in a condensed phase (liquid or solid), and special experiments have shown[13-17] that the gas-phase process may make a contribution, sometimes very substantial, to the total rate of decomposition.

An extremely important discovery for understanding the mechanism of the gas-phase decomposition of cyclic nitramines has been the intermediate formation of nitrogen dioxide[14,16,18], which can reasonably be interpreted in terms of the above mechanism for dialkylnitramines, with rupture of the $N-NO_2$ bond as the first stage[14,17]. Among the decomposition products of hexogen have been detected not only nitrogen dioxide but also nitrogen, nitrous and nitric oxides, carbon monoxide and dioxide, water, formaldehyde, hydrogen cyanide, ammonia, formic acid, hydroxymethylformamide, 1,2-dihydro-1,3,5-triazine, trimethylamine nitrate, and a polymer $(CH_2N-CHO)_n$.[13,14,16,18]. Mass-spectrometric detection of still other compounds has been reported[18], but they could not be identified unambiguously (in all the above studies decomposition took place in both gaseous and condensed phases).

A scheme suggested[17] for the gas-phase decomposition of hexogen



$$\rightarrow O_2N-\dot{N}-CH_2-NH-CHO + N_2 + CH_2O,$$
$$O_2N-\dot{N}-CH_2-NH-CHO \rightarrow N_2O + \dot{C}HOH-NH-CHO,$$
$$\dot{C}HOH-NH-CHO \rightarrow CH_2OH-NH-CHO,$$
$$CH_2O + NO_2 \rightarrow CO + CO_2 + NO + H_2O,$$
$$CH_2OH-NH-CHO \rightarrow \text{Polymerisation products},$$
$$CH_2OH-NH-CHO \rightarrow CH_2(NH-CHO)_2 + H_2O + CH_2O,$$
$$CH_2OH-NH-CHO + CH_2O \rightarrow (CH_2)_3N + CO_2 + H_2O,$$

shows good agreement with the composition of the pyrolysis products, but cannot be regarded as strictly proved. In particular, ring fission may occur in the first stage[18] giving formaldehyde, but this suggestion was not accompanied by a detailed scheme, and no clear distinction was made between processes taking place in gaseous and condensed phases.

If nevertheless we take the mechanism with rupture of the $N-NO_2$ bond as the most probable for gas-phase pyrolysis, we must expect that the activation parameters for the decomposition of hexogen will be closely similar to those for the above dialkylnitramines (Table 1). However, the activation energy and the pre-exponential factor has been given respectively as[15] 34.1 kcal mole^{-1} and 3.14×10^{13} s^{-1}, and also[19,20] as 30.0 and $10^{11.7}$. It is difficult to explain the discrepancy in these values and their appreciable departure from those for the pyrolysis of dialkylnitramines. Only two comments must be made: papers on the gas-phase pyrolysis of hexogen do not indicate whether any heterogeneous contribution to the kinetics (wall effect) is excluded; furthermore, the technique[15] of differential scanning calorimetry measured the kinetics in the later stages, after 96.5% conversion, i.e. in the presence of a large quantity of decomposition products, the influence of which on hexogen has not been specially studied.

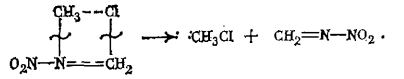
Clarity is introduced into this problem by a study[21] in which the activation energy and the pre-exponential factor for the gas-phase decomposition of hexogen have been found to be 35.0 kcal mole^{-1} and $10^{13.5}$ s^{-1}, almost the same as in Ref. 15. However, this work shows[21] that the reaction is inhibited by nitric oxide, from which it may be suggested that the above activation parameters represent not simply the primary decomposition step but a totality including secondary reactions. For the inhibited decomposition of hexogen the activation energy is 40.4 kcal mole^{-1} and the pre-exponential factor $10^{15.58}$ s^{-1},[21] values in excellent agreement with those in Table 1. They can be regarded as a strong argument in support of a mechanism of the gas-phase pyrolysis of hexogen involving rupture of an $N-NO_2$ bond as primary step.

From a detailed analysis of possible schemes for the decomposition of octogen based on published information it has been concluded[22] that the primary step is most probably homolytic rupture of an $N-NO_2$ bond, for which the activation energy and the pre-exponential factor were estimated as 46.2 kcal mole^{-1} and $10^{16.2}$ s^{-1}. The Reviewers regard these values merely as tentative, for implausible postulates had to be used[22] in their estimation. Thus the energy of dissociation of an $N-NO_2$ bond in octogen was determined from data for dimethylnitramine, but the pre-exponential factor was calculated from data for nitromethane and dinitrogen tetroxide. Other workers[19,20] give completely different parameters—32.0 kcal mole^{-1} and $10^{13.4}$ s^{-1}—for the gas-phase pyrolysis of octogen. As with hexogen, we find it difficult to explain such a marked scatter in values obtained by different workers.

In conclusion it is relevant to mention a short paper[23] expressing the interesting idea that the kinetics of the thermal decomposition of nitramines should depend on the geometrical configuration of the nitramino-group. Inspection of the experimental results shows that, if this group is

planar (dialkylnitramines, etc.), the activation parameters should be 40.9 kcal mole^{-1} and $10^{14.1}$ s^{-1}; but if it is pyramidal (hexogen, etc.) 37.8 kcal mole^{-1} and $10^{14.1}$ s^{-1}. This aspect merits further study and in particular quantum-chemical calculations.

We have been considering the thermal decomposition of compounds containing no reactive functional group other than nitramino. An investigation[24] of the pyrolysis of methylchloromethylnitramine $CH_3N(NO_2)CH_2Cl$ has shown that introduction of the chlorine atom has lowered significantly the thermal stability of dimethylnitramine and appreciably changed the kinetics of thermolysis, which is now definitely autocatalytic. The reaction is influenced appreciably by the addition of nitric oxide and inert gases (nitrogen, neon), which suggests[24] the presence of chain processes. It is significant that chloromethane and hydrogen chloride were detected among the decomposition products, and special experiments showed that the latter was the autocatalyst. Chloromethane may be formed in a unimolecular primary stage involving production of a cyclic activated complex:



This hypothesis is supported by the low pre-exponential factor $10^{10.5}$ s^{-1} of the first stage, whose activation energy is 30.7 kcal mole^{-1}.

III. DECOMPOSITION IN THE LIQUID PHASE

At the present time we are still far from having a general kinetic picture of the liquid-phase decomposition of nitramines. Moreover, there is no single nitramine whose mechanism of liquid-phase decomposition could be regarded as reliably established, although dozens of papers have appeared on this topic. It therefore appears advisable to discuss published results for each compound separately.

1. Hexogen

The thermal decomposition of hexogen (1,3,5-trinitro-1,3,5-triazacyclohexane, m.p. 205 °C) has been studied especially intensively during recent years, although Robertson's pioneering work was undertaken as early as the 1940s.[25,26] Essentially two main lines of attack—analysis of decomposition products and measurement of kinetic parameters—have been adopted in all investigations aimed at elucidating the mechanism and measuring the thermal stability of hexogen (this applies to all nitro-compounds). Unfortunately, neither of these approaches, despite their undoubted usefulness, provides an unambiguous interpretation of the reaction mechanism, mainly because kinetic investigations provide information only on the rate-determining steps—and then for not very complicated molecules—whereas the final products are mostly formed as a result of diverse secondary reactions. It is therefore to be expected that future progress in this field will involve the use of modern methods for identifying and studying intermediate reactive species (electron spin resonance, chemical polarisation of nuclei, spin traps).

The above work[25,26] detected the formation of nitric and nitrous oxides, nitrogen, hydrogen, carbon monoxide and dioxide, water, and formaldehyde. Table 2 gives as example the quantitative composition of the decomposition products. These are formed in somewhat different proportions when decomposition is conducted in solution in dicyclohexyl phthalate and trinitrotoluene.

The paper[14] first reporting the detection of nitrogen dioxide is extremely important: unlike the substances in Table 2, this may be a primary reaction product. Subsequently other products have been detected—hydrogen cyanide[14], hydroxymethylformaldehyde[16], formic acid, ammonia, trimethylamine nitrate[17], 1,2-dihydro-1,3,5-triazine, vinylnitramine (the peak in the mass spectrum having $m/e = 88$, which has been attributed to the structures $(CH_2)_2NNO_2$, $CH_2:CHNHNO_2$, and $CH_3CH:NNO_2$),[18] and also several other compounds, for which the empirical formulae

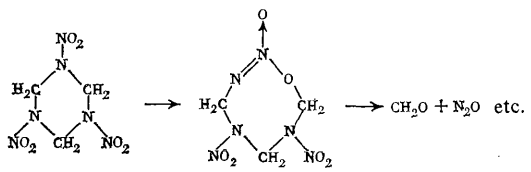
$$C_2H_4N, \quad C_2H_4N_2, \quad CH_2N_2O_2, \quad C_3N_3H_4, \quad C_3N_3H_5, \quad C_2H_4N_3O_2,$$
$$CH_2N_3O_4, \quad C_3H_4N_4O_2, \quad C_2H_4N_4O_3, \quad C_2H_4N_4O_4$$

have been proposed[27] on the basis of the mass spectra (we must repeat here that in most cases the decomposition was studied under two-phase conditions, with simultaneous occurrence of gas-phase and liquid-phase reactions).

Table 2. Products of the liquid-phase decomposition of hexogen (moles mole^{-1} hexogen).[26]

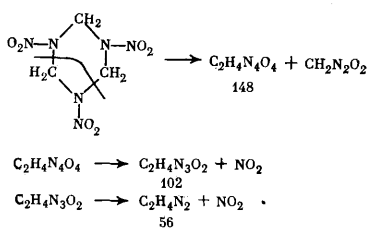
Temp.	NO	N_2O	N_2	H_2	CO	CO_2
225° C	0.54	0.98	1.16	0.09	0.40	0.48
267° C	0.75	0.76	1.03	0.06	0.29	0.44

The first ideas on the mechanism of the liquid-phase decomposition of hexogen were expressed by Robertson[26,14]:

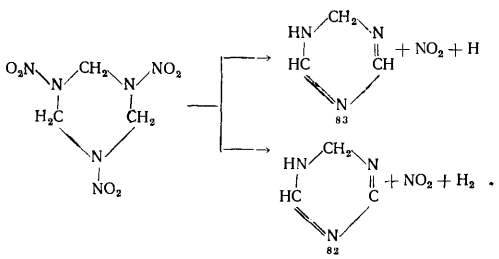


This scheme provides a reasonable explanation of the appearance of formaldehyde and nitrous oxide, but excludes the possibility of rupture of an N–NO_2 bond in the first stage, since nitrogen dioxide was not found. Although this product has since been detected[14,18,27], its kinetic behaviour with variation in the volume of the reaction vessel and in the weight of starting material differs from that of nitrous oxide and carbon dioxide[14]. From this it was concluded[14] that these products are formed under different conditions—nitrogen dioxide in gas-phase decomposition, but nitrous oxide and carbon dioxide in the liquid-phase reaction.

One of the possible mechanisms based on mass-spectrometric analysis of the decomposition products[27] involves cleavage of the ring (the numerals below the formulae indicate the masses of the ions detected in the mass spectrum):



However, these workers[27] assume a mechanism with separation of nitrogen dioxide without ring fission:



A similar mechanism was based by other workers[18] on the detection of 1,2-dihydro-1,3,5-triazine, although they examined the decomposition of hexogen only in gaseous and solid phases.

Before considering the mechanism of the liquid-phase decomposition of hexogen we note that the thermal stability was assessed qualitatively by differential thermal analysis[28]. The first kinetic investigation, showing a first-order reaction, was made by Robertson[26], who determined the kinetic parameters. However, later workers have obtained different results: thus over the range of degrees of conversion 10–80% the order appears[29] to be 1.36. A still more complicated picture has been observed[15], with an order of reaction 0.84 at degrees of conversion of 20.7–77%, followed by a sharp decrease, and then an increase to 0.94 at 96.5% conversion. Such complicated behaviour can be partly explained by the above two-phase character of the process, but the most important factor is most probably the complexity of the reaction itself, so that changes in experimental conditions lead to appreciable differences in kinetic behaviour. We may also mention the view[30] that the thermal decomposition of hexogen is autocatalytic.

Table 3. Activation parameters for the thermal decomposition of hexogen in the melt.

Method*	ΔT, °C	E_a, kcal mole^{-1}	A, s^{-1}	Ref.
Manometric	213–299	47.5±2.0	$10^{18.5}$	[26]
DSC	—	67.4±3.0	—	[31]
DTA	—	—	$10^{18.2}$	[32]
GChr	—	48.7	$1.7 \cdot 10^{19}$	[14]
DSC	206–252	48.2–53.0 **	($10^{18.8}$–$10^{20.3}$ **)	[29]
DSC	210–261	45.2±0.4	—	[33]
DSC	—	43.1	$2.44 \cdot 10^{16}$	[15]
DSC (isothermal)	204–225	41±1	—	[34]
DSC (non-isothermal)	—	42±3	—	[34]

*DSC = differential scanning calorimetry; DTA = differential thermal analysis; GChr = gas chromatography.
**Depending on choice of formula for calculation.

Table 3 shows quite good agreement among values obtained by different workers for the activation parameters of the liquid-phase decomposition of hexogen. With regard to the divergence shown by Ref.31, it may be noted that values given in this paper for other substances also differ appreciably from general published values. Furthermore, the temperature range of the measurements is not indicated[31], so that it is not very clear whether a hexogen melt was actually studied (this applies also to measurements under non-isothermal conditions in Ref.34).

The thermal decomposition of liquid hexogen is obviously complicated, and is accompanied by the formation of reactive intermediate species responsible for diverse secondary processes. It therefore appears quite natural to investigate the decomposition in solution, when bi- and ter-molecular secondary reactions are slowed down in comparison with the unimolecular decomposition of the initial compound.

Table 4. Activation parameters for the thermal decomposition of hexogen in solution.

Solvent	c*, %	ΔT, °C	E_a, kcal mole^{-1}	A, s^{-1}	Ref.
Dicyclohexyl phthalate	2–5	201–280	41.0	$10^{15.46}$	[26]
Trotyl	2–5	194.5–281	41.5	$10^{15.55}$	[26]
Convalex-10**	20	—	48.4	—	[31]
Trotyl	—	166–184	36.9±2.9	$10^{13.9\pm1.4}$	[36]
Benzophenone	—	—	37.8	$10^{14.5}$	[36]
m-Dinitrobenzene	—	160–200	39.7	$10^{14.3}$	[35]

*c = concentration of solution.
**Polyphenyl ether.

Appreciable autocatalysis is observed in dilute solution[26,35], in contrast to the melt. The induction period becomes shorter with rise in temperature, and completely disappears above 250 °C. The reaction is slower in solution than in the melt. Activation parameters in solution, determined from the initial portions of the kinetic curves on the assumption that a first-order equation is obeyed here, show good agreement among various workers (Table 4) with the exception of Ref.31. Another worker[36] did not observe autocatalysis in the thermal decomposition of hexogen: a first-order equation was satisfied throughout. The probable reason is that the experiments were conducted in relatively concentrated solutions, as first order is observed in the melt. It must therefore be expected that the induction period will become shorter with increase in concentration. This worker[36] noted also that products of the decomposition of hexogen are able to decompose trinitrotoluene. In this respect the latter is not the optimum solvent, although Table 4 shows that this does not affect the overall kinetic results.

The autocatalytic character of the thermal decomposition of hexogen in solution is most simply explained as above for the gas-phase breakdown of dimethylnitramine: on the hypothesis of a series of consecutive reactions. With rise in temperature the induction period may gradually diminish, and then completely disappear, as was observed by Robertson above 250 °C.[26]

An appreciable similarity in kinetic behaviour is evident between hexogen in solution and dimethylnitramine—the simplest secondary nitramine—in the gas phase, with slight acceleration and similar activation parameters (we have already noted a difference of 3 kcal mole^{-1} in the activation energies for the decomposition of these two compounds[23], attributed to a difference in the geometrical configuration of the nitamino-groups; however, this difference has little significance for our discussion, as the determination of activation energy in such experiments usually involves an error of 1–2 kcal mole^{-1}). Since the main features of the

mechanism of the decomposition of dimethylnitramine—primarily rupture of the $N-NO_2$ bond as the rate-determining stage—have been quite reliably established, the mechanism of the pyrolysis of hexogen in the liquid phase can reasonably be interpreted on the same basis, especially as such a hypothesis is supported by analysis of the decomposition products[18,27]. The increase in the rate of decomposition with solution concentration, passing to the melt in the limit, can reasonably be explained by an increasing contribution to the overall kinetics by bi- and ter-molecular secondary reactions, as noted above. The kinetic parameters (in particular those in Table 3) must then be regarded as overall values, not representing any particular elementary stage, which incidentally is supported by the high pre-exponential factors uncharacteristic of truly unimolecular reactions.

Robertson[26] suggested a chain mechanism for the thermal decomposition of hexogen in the melt. However, his experimental results[26] indicate that the length of the chain would be 1.31 and 2.96 at 205 and 273 °C respectively. Therefore we can hardly regard this as a chain process, and it is simpler to apply the concept of successive stages, which are eliminated with dilution of the solution.

As already stated, ideas on alternative mechanisms for the decomposition of hexogen assume in effect ring cleavage either following[26] or in the absence of[27] rearrangement. In the Reviewers' opinion, however, the composition of the products can provide only an indirect argument in support of these mechanisms, for they may be entirely formed in secondary stages, perhaps after rupture of an $N-NO_2$ bond. Furthermore, ring fission in primary stages will be expected to have activation parameters differing substantially from those for a mechanism with rupture of this bond. Nevertheless, as already stated, the decomposition of hexogen in solution is kinetically similar to that of dimethylnitramine in the gas phase.

Thus, of the two possibilities for the liquid-phase decomposition of hexogen, we prefer the radical mechanism with rupture of an $N-NO_2$ bond. In our view it is consistent with all the available experimental facts, whereas mechanisms involving ring fission show poor agreement with kinetic data for decomposition in solution. On the other hand, the choice between different mechanisms cannot be regarded as finally settled, since there is no direct evidence to prove or disprove a particular mechanism. In particular, the increase in reaction velocity on passing to the melt can be explained by a change in mechanism, with the possibility of bimolecular interaction between hexogen molecules in the melt. This aspect has been considered by Stals[37] in terms of quantum chemistry (applied to the decomposition of solid hexogen).

2. Octogen

Octogen (1,3,5,7-tetranitro-1,3,5,7-tetra-azacyclo-octane) resembles hexogen, so that it is not surprising that it behaves similarly on thermal decomposition, although quantitatively it is more thermostable: according to differential thermal analysis[28] octogen and hexogen undergo intense decomposition at 260 and 215 °C respectively. The decomposition of octogen has been studied also by differential scanning calorimetry[29]: this paper gave degrees of decomposition corresponding to the maximum on the scanning curve as a function of rate of heating, but the kinetic parameters had not been calculated.

The first detailed kinetic investigation of the thermal decomposition of octogen was reported by Robertson in the paper already mentioned[26]: he found a first-order reaction, and traced an analogy between hexogen and octogen. Table 5 collects existing data on the liquid-phase decomposition of the latter. Another study[15] by differential scanning calorimetry indicated an order of 0.6 at degrees of decomposition of 15.5–97.7%, but the experimental method was such that reaction took place in both gas and liquid phases. In Table 5 such large activation energies as 228 kcal mole^{-1} [31] are improbable and uncharacteristic not only of nitramines but also of nitro-compounds in general. The remaining very few values show quite good mutual agreement.

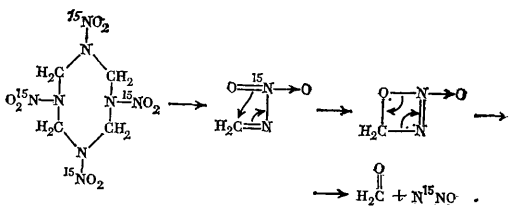
Table 5. Activation parameters for the thermal decomposition of octogen in the melt.

Method	ΔT, °C	E_a, kcal mole^{-1}	A, s^{-1}	Ref.
Manometric	271–314	52.7	$10^{19.7}$	[26]
–	—	52.7	—	[31] *
–	—	59.0	—	[31] **
DSC	—	228±24	—	[31]
DSC	—	—	$10^{18.1}$—$10^{18.9}$ ***	[32]
DSC	271–285	51.3	$6.4 \cdot 10^{18}$	[38]
DSC	—	44±10	—	[34]

*Unpublished results of Johnston, quoted in Ref.31.
**Unpublished results of Lind, quoted in Ref.31.
***Depending on method of calculation.

As with hexogen, useful information can be obtained from decomposition in solution. In Convalex-10 (a polyphenyl ether) the activation energy was 50.3 kcal mole^{-1}.[31] A more detailed investigation[35] in *m*-dinitrobenzene solution established the slightly autocatalytic character of decomposition (as with hexogen in solution and dimethylnitramine in the gas phase). The activation energy and the pre-exponential factor were respectively 44.9 kcal mole^{-1} and 10^{16} s^{-1}.

The composition of the gaseous decomposition products from octogen was about the same as from hexogen[26]. The isotopic composition of the gaseous products from octogen labelled with nitrogen-15 in the nitro-group was the same ($^{14}N^{15}NO$, ^{15}NO, $^{14}N^{15}N$, $HC^{14}N$) below and above the melting point (over the range 230–285 °C).[39] It has thus been reliably established that nitric oxide is formed only from a nitro-group, nitrogen and nitrous oxide from a nitro-group and a nitrogen atom of the ring, and hydrogen cyanide only from a cyclic nitrogen atom. From these results it was concluded[39] that the decomposition of octogen does not involve rupture of $N-NO_2$ bonds and perhaps involves the stages



Although this scheme appears reasonable from our point of view and supports a reaction mechanism involving ring cleavage in the rate-determining stage, we nevertheless consider that it does not disprove, and moreover does not even contradict, a radical mechanism with $N-NO_2$ bond rupture in the first step. Indeed, nitrogen dioxide may attack another octogen molecule at an amino-nitrogen atom (a similar scheme has been given above for dimethylnitramine), and nitrous oxide and nitrogen having the observed isotopic composition could be formed by a series of secondary processes. Oxidation by nitrogen dioxide of formaldehyde resulting from the decomposition of octogen yields not nitrous oxide[39] but nitric oxide[40], which would of course have the isotopic composition ^{15}NO.

As with hexogen, an unambiguous interpretation of the mechanism of the liquid-phase decomposition of octogen is at present impossible. However, in view of the close analogy between these nitramines (similar structure, behaviour on thermal decomposition both in the melt and in solution, and composition of reaction products), we are inclined to support a radical mechanism with rupture of an $N-NO_2$ bond in the first stage, especially as it is indicated also by a thorough analysis[22] of possible decomposition schemes (though this was undertaken for gas-phase pyrolysis). The greater activation energy of decomposition of octogen than of hexogen can be explained (in terms of the ideas in Ref. 23) by differences in stability of $N-NO_2$ bonds depending on the geometrical configuration of the nitramino-group (planar, pyramidal, etc.).

3. Dinitropiperazine and Dinitroimidazolidine

Information on the thermal decomposition of other cyclic nitramines has appeared quite recently[40,41]. The kinetics of the decomposition of *NN'*-dinitropiperazine and *NN'*-dinitroimidazolidine (1,3-dinitro-1,3-diazacyclopentane) are fairly complicated: in the melt slight autocatalysis was observed by one group of investigators[40], but not by the other group[41], who worked at higher temperatures. On the other hand, the latter observed[41] that the ratio of the initial weight taken to the volume of the reaction vessel m/V influenced the kinetics, as also in solution did the concentration or at constant concentration this ratio. Thus, although as with other compounds data obtained in dilute solution are most convenient to interpret, there is no certainty that the rate constants obtained represent solely the primary step in decomposition.

Table 6. Activation parameters for the thermal decomposition of *NN'*-dinitropiperazine and *NN'*-dinitroimidazolidine in the liquid phase[40,41].

Nitramine	State	ΔT, °C	E_a, kcal mole^{-1}	A, s^{-1}
NN'-Dinitropiperazine	melt	216—250	47.4	$10^{17.3}$
NN'-Dinitropiperazine	soln.	130—245	45.8	$5.68 \cdot 10^{15}$
NN'-Dinitroimidazolidine	melt	135—200	37.1	$8 \cdot 10^{13}$
NN'-Dinitroimidazolidine	soln.	120—210	37.9	$9.53 \cdot 10^{13}$

Activation parameters determined by the two groups over different temperature ranges sometimes differed appreciably, but quite satisfactory agreement was obtained when both sets of results[40,41] were included in a single Arrhenius plot (Table 6). Furthermore, varying the solvent (*m*-dinitrobenzene, 1,3,5-trinitrobenzene, 2,4,6-trinitrotoluene) has no appreciable influence on the kinetics. Both groups interpret the results, as with hexogen and octogen, in terms of a radical mechanism involving rupture of an $N-NO_2$ bond in the first step. Comparison of the results in Table 6 for reactions in solution shows that activation parameters for the thermolysis of dinitropiperazine and dinitroimidazolidine are identical, within the limits of experimental error, with those for octogen and hexogen respectively.

Several general conclusions can be drawn from all these results on the influence of certain factors on the thermal stability of cyclic nitramines. Change in size of ring or number of nitro-groups apparently does not affect thermal stability directly. Indeed, octogen and dinitropiperazine are respectively eight- and six-membered rings containing four and two nitro-groups: and the less thermostable pair hexogen and dinitroimidazolidine are six- and five-membered rings with three and two nitro-groups. Nor does the distance between the nitramino-groups play an appreciable part: in octogen and dinitropiperazine they are separated by one and two methylene groups respectively, but the difference in activation energy in solution does not exceed 1 kcal mole^{-1}. With respect to thermal stability it is obviously most significant that change in molecular structure (ring size or number of nitramino-groups) entails a change in strength of the $N-NO_2$ bond perhaps owing to the above change in geometrical configuration of the nitramino-group[23].

The most interesting result of an analysis[40] of the gaseous products of the thermal decomposition of dinitropiperazine and dinitroimidazolidine is that nitrous oxide is not produced from the former in solution. Thus it is not necessarily a product of the thermal decomposition of cyclic nitramines.

4. Tetryl and its Analogues

Tetryl (*N*-methyl-*N*,2,4,6-tetranitroaniline), together with trotyl and nitroglycerin, was for many years a kind of model substance, from which the principal laws governing the thermal decomposition of explosives were elucidated. Thus Knowles[42], who was apparently the first to regard thermal decomposition as a method for assessing the chemical stability of explosives, worked with tetryl.

Investigation of the thermal decomposition of tetryl by differential thermal analysis showed[28] that it is less thermostable than many other explosives, including those considered above. Together with thermogravimetry these results indicate a two-stage reaction: at 162 °C the heat curve shows a sharp exothermic peak, which is followed at about 200 °C by a less marked second peak. Other workers[43] have observed exothermic peaks at 160 and 230 °C. Under somewhat different experimental conditions the same peaks have been observed[44] at 197 and 293 °C. Qualitative results have been published for the thermal decomposition of a mixture of 30% of tetryl and 70% of trotyl[45,46].

The first kinetic investigations of the thermal decomposition of tetryl have now become classics[1,2]. The reaction exhibits clearly developed autocatalysis, effected by picric acid formed in the reaction. It has since been established[47] that the rate of the liquid-phase decomposition comprises the rate of the first-order non-catalytic decomposition and that of a second-order autocatalytic reaction (first order with respect to tetryl and to the catalyst). This paper noted that calculation of catalytic rate constants must take into account the decrease in volume of the condensed compound during the reaction, as

such decrease causes an additional increase in catalyst (picric acid) concentration.

Table 7 compares results obtained for the thermal decomposition of tetryl by various workers, some of whom did not separate the stages and found gross values for the activation parameters (Table 8). All the results show good agreement: activation energies for the non-catalytic reaction lie in the range $E_a = 37.5 \pm 2.5$ kcal mole^{-1}, and the pre-exponential factors $A = 10^{14.5 \pm 1.5}$ s^{-1}; for the catalytic reaction $E_a = 37 \pm 1.5$ kcal mole^{-1} and $A = 10^{15 \pm 0.5}$ s^{-1}. Some values in Table 8 are exceptions: apart from the absence of separation of catalytic from non-catalytic stages, Roginskii's miscalculations[3,54] were based on extremely limited experimental results[1,2]; we have already noted that values in Ref. 31 show poor agreement with those obtained by other authors; and the results in Ref. 33 were obtained over a temperature range of only 4 deg.

Table 7. Activation parameters for the thermal decomposition of tetryl in the melt.

Method	ΔT, °C	Non-catalytic		Autocatalytic		Ref.
		E_a, kcal mole^{-1}	A, s^{-1}	E_a, kcal mole^{-1}	A, s^{-1}	
Manometric	211—260	38.4	$10^{15.4}$	—	—	[48]
Gravimetric	131.9—163.7	34.9	$10^{12.9}$	—	—	[49]
Calorimetric	130—155	36.0	$10^{13.8}$ *	38.0	$10^{15.6}$ *	[47]
Manometric	140—160	35.2	$10^{13.5}$	37	—	[48]
Manometric	140.3—164.9	40	10^{16}	35.5	$10^{14.5}$	[51]
Manometric**	150—175	35.9	$10^{13.5}$	—	—	[52, 53]

*Converted from values measured in min^{-1}.
**Experiments conducted in dinitrobenzene solution.

Table 8. Activation parameters for the thermal decomposition of tetryl in the melt.

Method	ΔT, °C	E_a, kcal mole^{-1}	A, s^{-1}	Ref.
Gas analysis	129.9—138.6	60.0	$10^{27.5}$	[3.52] *
Gas analysis	140—150	55.5	$10^{24.5}$	[3.53] **
Gas analysis	150—175	35	—	[42]
DSC	—	54.9	—	[30]
DSC***	—	33.5	—	[31]
DSC	—	—	$10^{15.2}$—$10^{15.5}$	[31]
DSC	170—174	58	—	[32]

*Calculated from experimental results in Ref. 1.
**Calculated from experimental results in Ref. 2.
***Experiments conducted in solution in Convalex-10.

The above mean activation parameters for the liquid-phase decomposition of tetryl agree in general with those for the other nitramines discussed, although tetryl decomposes more rapidly and has a lower activation energy, which may have several causes. Tetryl is an aromatic nitramine, and the trinitrophenyl group may influence the electronic structure of the nitramino-group, enhancing its reactivity. Furthermore, the rate of the non-catalytic stage increases with the m/V ratio[50], which implies that the reaction is catalysed not only by the condensed product (picric acid) but also by gaseous products. The activation parameters also depend on this ratio: with increase in m/V from 0.80 to 35.35 mg cm^{-3} the activation energy of the non-catalytic stage increases from 35.2 to 42.2 kcal mole^{-1}, and the pre-exponential factor from $10^{13.5}$ to $10^{17.5}$ s^{-1}.[50] Thus this rate constant is not a true but an effective value, which includes a contribution by reactions involving gaseous products. Hence the activation parameters in Table 7 (and in general those of the other nitramines considered) represent only to a first approximation the primary stage of decomposition (the data from Ref. 50 in Table 7 apply to $m/V = 0.80$ mg cm^{-3}).

Several analyses have been made of the gaseous products of the thermal decomposition of tetryl[50,51,43]. Some workers detected nitrogen dioxide, nitric oxide, and carbon dioxide and monoxide[48,49]; others found methane together with nitrogen dioxide, nitric oxide, and nitrogen[43]; methyl nitrite and nitrate are also formed[53]. During decomposition the concentrations of nitrogen dioxide and nitric oxide pass through a maximum[50]. Together with the above tendency of nitramines to be oxidised by nitrogen dioxide, this suggests that such oxidation is responsible for the dependence of the rate of the non-catalytic stage on the m/V ratio.

Gaseous decomposition products are mostly formed in secondary stages, so that their analysis gives little information on the mechanism of the initial stages. In this respect condensed decomposition products have the greatest interest. One of them (picric acid) has been known for a long time[1,2]. Other condensed products—2,4,6-trinitroanisole and *N*-methyl-2,4,6-trinitroaniline—have also been found[51]. These conclusions have since been confirmed[55,56], together with the detection of small quantities of 2,4,6-trinitroaniline, 1,3,5-trinitrobenzene, *N*-methyl-*N*,2,4-trinitroaniline, and perhaps *N*,2,4,6-tetranitroaniline.

Table 9. Kinetics of the thermal decomposition of 2,6-$(NO_2)_2$-4-$R^1C_6H_2N(NO_2)R^2$ in dinitrobenzene solution[52,53].

R^1	R^2	ΔT, °C	10^5k, s^{-1} (at 160 °C)	E_a, kcal mole^{-1}	A, s^{-1}
OCH_3	CH_3	145—165	$1.78 \cdot 10$	32.1	$10^{12.44}$
CH_3	CH_3	150—170	$1.5 \cdot 10$	34.2	$10^{13.42}$
Cl	CH_3	145—165	9.6	33.7	$10^{13.11}$
Br	CH_3	155—175	9.2	33.8	$10^{13.41}$
NO_2	CH_3	150—175	5.5	35.9	$10^{13.50}$
NO_2	C_2H_5	144—165	$3.7 \cdot 10$	33.3	$10^{13.90}$
NO_2	n-C_3H_7	135—155	$6.6 \cdot 10$	32.7	$10^{13.30}$
NO_2	iso-C_4H_9	130—150	$1.75 \cdot 10^2$	33.5	$10^{14.16}$

The above close similarity between the activation parameters of the thermal decomposition of tetryl and other nitramines suggests identity of the first stage in their decomposition—rupture of an N—NO_2 bond—which is consistent with the formation of *N*-methyl-2,4,6-trinitroaniline among the decomposition products. This compound may be formed by detachment of a hydrogen atom from an adjacent molecule by an *N*-methyl-2,4-6-trinitrophenylamino-radical produced in the first stage. Additional evidence supporting rupture of an N—NO_2 bond in the first stage of decomposition was obtained by Stepanov et al.[52,53], who made a kinetic investigation of tetryl and several of its analogues of general formula 2,6-$(NO_2)_2$-4-$R^1C_6H_2N(NO_2)R^2$. With variation of R^1 the results (first five lines in Table 9) conform well to the correlation

$$\lg k = -(0.488 \pm 0.026)\sigma - (3.898 \pm 0.011)$$
$$(r = 0.996,\ S_y = 0.016,\ n = 5).$$

A different relation is satisfied with variation of R^2 (last four lines):

$$\lg k = -(7.825\pm0.240)\sigma^* - (0.556\pm0.032)E_s - (4.259\pm0.017)\ (r=0.999,\ r_1=0.961,\ r_2=0.849,\ S_y=0.025,\ n=4).$$

Thus increase in electron density on the amino-nitrogen atom of the nitramino-group increases the rate of thermal decomposition. Examination of possible decomposition schemes also led to the conclusion[52,53] that a radical scheme is most consistent with the kinetic data and the correlation analysis. From this and the published composition of the products the following mechanism was proposed[52] for the decomposition of tetryl [Ar = 2,4,6-$(NO_2)_3C_6H_2$]:

$$\begin{aligned}
&ArN(CH_3)NO_2 \rightarrow Ar\dot{N}CH_3 + NO_2\ ,\\
&Ar\dot{N}CH_3 + NO_2 \rightarrow ArN(CH_3)\dot{O} + NO\ ,\\
&Ar\dot{N}CH_3 + NO \rightarrow ArN(CH_3)NO\ ,\\
&ArN(CH_3)NO \rightarrow ArON{=}NCH_3\ ,\\
&ArON{=}NCH_3 \rightarrow ArOCH_3 + N_2\ ,\\
&ArN(CH_3)\dot{O} \rightarrow Ar\dot{N}H + CH_2O\ ,\\
&Ar\dot{N}H + NO \rightarrow ArNHNO\ ,\\
&ArNHNO \rightarrow ArN{=}NOH\ ,\\
&ArN{=}NOH \rightarrow ArOH + N_2\ ,\\
&CH_2O + NO_2 \rightarrow CO + CO_2 + H_2O + NO\ ,\\
&ArOCH_3 \xrightarrow{\text{hydrolysis}} ArOH\ .
\end{aligned}$$

Here we may refer again to the possible formation of $ArNHCH_3$ from $ArN(CH_3)\cdot$ by acceptance of a hydrogen atom from some molecule. Similarly $ArN(H)\cdot$ can accept hydrogen to form $ArNH_2$. Picric acid can be obtained by the hydrolysis not only of trinitroanisole but also of tetryl itself[42].

The nature of the autocatalysis has remained largely obscure. Decomposition of tetryl is accelerated not only by picric acid but also by sulphuric acid[1], whereas nitric and acetic acids have no catalytic effect, apparently because of their volatility. It was suggested[2] that picric acid acts as a protic catalyst; other workers[51] assumed that protonation occurs at the amino-nitrogen atom, but gave no evidence of the mechanism of catalysis. Moreover, it remains obscure why the thermal decomposition of tetryl but not of other nitramines is so strongly autocatalytic.

5. Substituted Dialkylnitramines

The present subsection examines the liquid-phase decomposition of compounds of general formula $R^1N(NO_2)R^2$, where R^1 and R^2 are substituted alkyl groups.

The kinetics of the thermal decomposition of bis-2,2-dinitropropylnitramine in 5% solution in *m*-dinitrobenzene at 145–196.2 °C is similar[57] to that of the gas-phase pyrolysis of dimethylnitramine, with slight autocatalysis and activation parameters characteristic of the nitramines already discussed: the activation energy is 39.7 ± 1.4 kcal $mole^{-1}$, and the pre-exponential factor $10^{15.7\pm0.7}$ s^{-1}. Hence it may be supposed that decomposition of this compound resembles that of the other nitramines, having a radical mechanism with primary rupture of an $N-NO_2$ bond.

Similar results have been obtained[58] for the thermal decomposition of *N*-nitro-γ-azavaleric acid at 180–220 °C. Appreciable autocatalysis was observed; for the initial stage the activation energy and the pre-exponential factor were respectively 42.08 kcal $mole^{-1}$ and $10^{14.72}$ s^{-1}. The decomposition products included acrylic acid, nitrosomethane, *N*-methylmethyleneimine, carbon monoxide and dioxide, water, nitrogen, and nitric and nitrous oxides. The kinetic parameters again indicate rupture of an $N-NO_2$ bond in the first stage, and the scheme

$$\begin{aligned}
&CH_3N(NO_2)CH_2CH_2COOH \rightarrow CH_3\dot{N}CH_2CH_2COOH + NO_2\ ,\\
&CH_3\dot{N}CH_2CH_2COOH \rightarrow CH_3\dot{N}H + CH_2{=}CHCOOH\ ,\\
&CH_3\dot{N}CH_2CH_2COOH \rightarrow CH_2{=}NCH_3 + \dot{C}H_2COOH\ ,\\
&CH_3N(NO_2)CH_2CH_2COOH + A \rightarrow CH_3N(NO_2)CH_2\dot{C}HCOOH\ ,\\
&CH_3N(NO_2)CH_2\dot{C}HCOOH \rightarrow CH_3\dot{N}NO_2 + CH_2{=}CHCOOH\ ,
\end{aligned}$$

was suggested to explain the composition of the products, where A is a hydrogen acceptor, e.g. NO_2. The remaining gaseous decomposition products may be formed by the oxidation of $CH_3N(H)\cdot$ and $\cdot CH_2COOH$ with nitrogen dioxide and by the breakdown of $CH_3N(NO_2)\cdot$.

The decomposition of many nitramino-carboxylic acids and their salts has been studied[59] by differential thermal analysis, thermal stability being assessed from the temperature corresponding to an exothermic peak. Although kinetic parameters were not determined, qualitative relations could be established between thermal stability and molecular structure. It was found in particular that the stability increases with the length of the aliphatic chain and with the p*K* of the acid. Thermal stability is influenced also by the position of the nitramino-group in the molecule.

Table 10. Kinetics of the thermal decomposition of $R^1N(NO_2)R^2$ in dibutyl phthalate solution[53].

R^1	R^2	Δ*T*, °C	10^5k, s^{-1} (at 210 °C)	E_a, kcal $mole^{-1}$	*A*, s^{-1}
CH_3	$(CH_2)_2COOCH_3$	200–230	2.89	40.4	$10^{13.77}$
CH_3	$(CH_2)_2CN$	190–230	2.57	41.9	$10^{14.43}$
CH_3	CH_2OCH_3	190–230	2.34	40.9	$10^{13.89}$
$(CH_2)_2COOCH_3$	$(CH_2)_2COOCH_3$	210–250	1.78	40.7	$10^{13.76}$
$(CH_2)_2CN$	$(CH_2)_2CN$	210–250	1.46	41.3	$10^{13.92}$
CH_3	$(CH_2)_2COOH$	200–230	3.40	40.8	$10^{14.03}$
$(CH_2)_2COOH$	$(CH_2)_2COOH$	200–240	4.05	40.8	$10^{14.07}$

A systematic investigation of the decomposition of several substituted dialkylnitramines in 5% solution in dibutyl phthalate has shown[53] that variation in the substituents has very little effect on the kinetics (Table 10), which is characteristic of the thermal decomposition of nitramines in general. Nevertheless, a correlation was obtained between structure and reactivity (except for the last two examples whose decomposition kinetics were apparently influenced by ionisation of the carboxyls):

$$\lg k = -(0.495\pm0.02)\ (\sigma^*_{R^1}+\sigma^*_{R^2}) - (4.34\pm0.01)\ (r=0.982,\ S_y=0.028,\ n=6).$$

As in the tetryl series the values of the activation parameters and the sign of the constant ρ* again support rupture of an $N-NO_2$ bond in the first stage.

Manometric and derivatographic methods have been used[60] for a kinetic study of the thermal decomposition of ferrocenylmethylnitramines $FcCH_2N(NO_2)R$ (where Fc = ferrocenyl and $R = CNCH_2CH_2$, $CH_3C(NO_2)_2CH_2CH_2$, $FcCH_2$) in 2% solution in dibutyl phthalate. The second of these compounds follows a first-order law up to 50% decomposition, but the other two show slight autocatalysis. Table 11 lists the kinetic parameters of the initial stages calculated on the assumption that they are described by a first-order equation. The activation parameters for decomposition of the latter two compounds are closely similar to those for other nitramines,

from which it was concluded[60] that they decompose with rupture of an N–NO_2 bond in the first stage. The cyanoethyl compound decomposes appreciably more rapidly, which is attributed[60] to a different mechanism: the first stage involves rupture not of an N–N but of a C–N bond.

Table 11. Kinetics of the thermal decomposition of $FcCH_2N(NO_2)R$.[60]

R	ΔT, °C	10^4k, s^{-1} (at 170 °C)	E_a, kcal mole^{-1}	A, s^{-1}
CH_2CH_2CN	160–180	1.29	42.9	$10^{17.26}$
$CH_2CH_2C(NO_2)_2CH_3$	180–200	$6.30\cdot10^{-2}$	36.8	$10^{12.96}$
$FcCH_2$	190–200	$3.16\cdot10^{-2}$	38.5	$10^{13.49}$

In the Reviewers' opinion, however, there are insufficient grounds for such a conclusion, and it is more reasonable to suppose that the cyanoethyl derivative, like the other nitramines, breaks down with rupture of the N–NO_2 bond as the rate-determining stage. This view can be supported by the absence of obvious differences between cyanoethyl and the other two substituents that could cause such a sharp change in reaction mechanism. The cyanoethyl derivative decomposes with slight autocatalysis, so that the observed rate constant evidently does not characterise solely the first step. In view of the narrow temperature range of the measurements, the observed activation parameters may therefore differ markedly from those representing the primary step. Furthermore, the value $E_a = 42.9$ kcal mole^{-1} in Table 11 is closely similar to those given above for other nitramines.

Derivatographic investigation of ferrocenylmethylnitramines[60] revealed several exothermic peaks, indicating that decomposition involved a series of consecutive reactions, but their nature was not studied.

Study of the decomposition of 2,4,6-trinitro-2,4,6-triazaheptamethylene diacetate by differential scanning calorimetry[33] gave the activation energy 53 ± 5 kcal mole^{-1}. The fewness of the experimental results makes any interpretation of this value difficult.

6. Dina

Dina (nitraminodiethyl dinitrate) contains different reactive functional groups—nitrimino and two nitrato—each of which can influence the kinetics of thermal decomposition in its own way.

Kinetic study by manometric, gravimetric, and calorimetric methods with small quantities in the reaction vessel (in the manometric experiments $m/V = 10^{-4}$ g cm^{-3}) at 150 to 170 °C showed[61] a first-order reaction with $E_a = 45.0$ kcal mole^{-1} and $A = (3.8–4.8) \times 10^{18}$ s^{-1} (depending on the mode of measurement). These kinetic parameters were used[62] to calculate those of thermal explosion. Good agreement was found between calculation and experiment.

However, later research showed[63] that the decomposition of dina has more complicated kinetics: with sufficiently high m/V ratios at sufficiently low temperatures the reaction is autocatalytic, the more strongly so the higher the ratio and the lower the temperature. With decrease in the ratio and rise in temperature, however, autocatalysis becomes increasingly weaker, and finally disappears altogether. Thus with $m/V = (5–10) \times 10^{-4}$ g cm^{-3} at 160 °C the rate of decomposition falls monotonically during the reaction, but more slowly and not in conformity with a first-order law: in other words, if the process is described formally by a first-order equation, the observed rate constant increases during the reaction. The first order reported in Ref.61 was apparently due precisely to the use of low m/V ratios (10^{-4} g cm^{-3}) at high temperatures (150–170 °C).

The dependence of the rate of decomposition of dina on the m/V ratio indicates the participation of a gaseous product in the rate-determining stage. This is most probably nitrogen dioxide, which, as we have noted, tends to oxidise the nitramino-group. Indeed, with increase in the ratio and fall in temperature (i.e. on passing to conditions of appreciable autocatalysis) the content of this gas among the reaction products diminishes[63], which can be attributed to an increasing role of redox processes involving it under conditions ensuring autocatalysis.

Detailed experiments with additions of water revealed[63] that the autocatalysis is probably largely due to acid hydrolysis of dina, which becomes more intense with accumulation of water, nitrogen dioxide, and nitric acid. In this respect dina resembles many other nitric esters, in particular nitroglycerin. However, there is no complete analogy with the latter, since the above redox processes play an important part in the decomposition of dina, which also contains a nitramino-group readily oxidised by nitrogen dioxide and perhaps nitric acid.

The complicated character of the thermal decomposition of dina probably prevents determination of the kinetic parameters of the first step even from the initial rates; the rate constants of the initial stage of decomposition themselves are obviously effective values, and depend on the experimental conditions. It is therefore not surprising that the activation parameters obtained[63] (on the assumption of a first-order equation) differed somewhat from those in Ref.61: with $m/V = (5–20) \times 10^{-4}$ g cm^{-3} at 100–170 °C, the activation energy and the pre-exponential factor were respectively 42.0 kcal mole^{-1} and 10^{17} s^{-1}; with $m/V = (6–12) \times 10^{-2}$ g cm^{-3} at 70–90 °C the corresponding values were 41.5 and 10^{16}.

Subsequent research has confirmed and developed the earlier results[61,63]. The kinetics of the decomposition of dina has been studied[64] calorimetrically with very high m/V ratios (with the reaction vessel almost completely filled): the reaction velocity exceeds some hundredfold the value when $m/V = 10^{-4}$ g cm^{-3}, which is fully consistent with the accelerating role of gaseous reaction products. Kinetic curves for the evolution of heat under isothermal conditions between 103 and 111 °C are complicated with two maxima, which indicates the occurrence of two processes separated in time and responsible for the acceleration of decomposition; they have activation energies of 34 and 32 kcal mole^{-1}. The observed activation energy diminishes non-uniformly with the degree of decomposition over the range $\eta = 0.1–0.45$, after which it remains unchanged at 32 kcal mole^{-1}. The conclusion[64] that two processes accelerate the thermal decomposition of dina is consistent with a contribution[63] by acid hydrolysis and redox stages to this reaction.

The kinetics of decomposition has also been investigated[65] calorimetrically over the pressure range 0.05–5 atm. A rise in pressure favours dissolution of gaseous products in liquid dina, and according to the above discussion should accelerate the reaction. This is indeed observed, with the activation energy and pre-exponential factor (45.0 kcal mole^{-1} and 3×10^{18} s^{-1}), obtained at 0.05 atm on the assumption of a first-order reaction, showing good agreement with the above values[61]. Rise in pressure to 1 atm is accompanied by

gradual increase in the contribution by gaseous products to the overall reaction, with a consequent fall in the activation energy to 35 kcal mole^{-1} and in the pre-exponential factor to 2.5×10^{13} s^{-1}. Further rise in pressure to 5 atm does not affect the activation energy, but the rate constant continues to increase somewhat (owing to the pre-exponential factor). The kinetic parameters for 1 atm were used[65] to calculate parameters of thermal explosion in good agreement with experimental values.

Thermographic investigation of the decomposition of dina gave heating curves[66] with two exothermic peaks, indicating as before[64] two time-separated reactions accelerating the decomposition. A computer simulation was based on the simplified formal scheme

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \quad (1)$$

$$A + B \xrightarrow{k_3} 2B + C \quad (2)$$

Stage (1) represents a series of consecutive reactions (perhaps B = NO_2) and stage (2) an autocatalytic process (perhaps acid hydrolysis). Activation energies E_1–E_3 corresponding to the rate constants k_1–k_3 were obtained of 43.8, 28.6, and 28.7 kcal mole^{-1}, with corresponding pre-exponential factors A_1–A_3 of 1.1×10^{18}, 4.3×10^9, and 4.3×10^{11} s^{-1}. The kinetic parameters corresponding to the stage A → B are closely similar to values observed previously[61,63], and those corresponding to the other two stages to values observed at high m/V ratios[64] and under high pressures[65].

The macrokinetic characteristics of the thermal decomposition of dina have been studied[67] also by impulse calorimetry.

It was suggested[63] that the primary stage in the thermal decomposition of dina, as of other nitric esters, involves rupture of the O–NO_2 bond. However, it must be recalled that in the gas phase simple nitric esters and nitramines have closely similar activation parameters: i.e. nitrato- and nitramino-groups are similar in reactivity. Furthermore, the above activation parameters for dina[61,63], though not fully representing the primary step, are nevertheless closely similar to corresponding values for other nitramines. Thus the nature of the first stage in the thermal decomposition of dina remains an open question.

7. Nitramides and *N*-Nitrocarbamates

In 1955 White showed[68] that heating *N*-n-butyl-*N*-nitroacetamide in tetrachloromethane solution at 77 °C for 15 h gives n-butyl acetate (in 75% yield) with acetic acid and but-1-ene (each in 23% yield) as well as nitrous oxide. This reaction was subsequently[69,70] extended to a wide range of nitramides $R^1N(NO_2)CO.R^2$ and *N*-nitrocarbamates $R^1N(NO_2)COOR^2$ (where R^1 = Alk and R^2 = Alk, Ar). By analogy with nitrosamides, which by that time had been studied in detail (for reference see Refs.68–70), a reaction mechanism with intermediate formation of a diazoxy-ester was suggested:

$$R^1N(NO_2)C(O)R^2 \rightarrow [R^1N{=}N^+(O^-)OCR^2] \cdot$$

This intermediate is unstable, and can decompose in two ways:

$$[R^1N{=}N^+(O^-)OCR^2] \rightarrow R^1OC(O)R^2 + N_2O$$

$$[R^1N{=}N^+(O^-)OCR^2] \rightarrow R^2COOH + N_2O + \text{Alkene},$$

where the alkene corresponds to detachment of a hydrogen atom from R^1. Thermal decomposition is accompanied by isomerisation. For example[70] *N*-isobutyl-3,5-dinitrobenzonitramide in tetrachloromethane solution at 76 °C gives not only isobutyl 3,5-dinitrobenzoate but also the corresponding s-butyl and t-butyl esters in respective yields of 16% and 1–3% relative to the isobutyl compound. A weighty argument in support of the suggested mechanism was that the diazoxy-ester was obtained *in situ* by an independent method, and on decomposition gave the same products as did the corresponding nitramide.

Table 12. Rate constants for the thermal decomposition of nitramides, nitrosamides, and nitrocarbamates[71].

N-Nitro-compound	Solvent	Temp., °C	k, s^{-1}
n-$C_4H_9N(NO)COCH_3$	xylene	90	$7.59 \cdot 10^{-3}$
$C_2H_5N(NO_2)COC_2H_5$	decane	90	$2.70 \cdot 10^{-4}$
n-$C_4H_9N(NO)COOCH_3$	dodecane	90	$4 \cdot 10^{-6}$
n-$C_4H_9N(NO_2)COOCH_3$	decane	90	$7.4 \cdot 10^{-8}$
iso-$C_3H_7N(NO)COCH_3$	xylene	60	$4.2 \cdot 10^{-3}$
s-$C_4H_9N(NO)COOCH_3$	dodecane	90	$2 \cdot 10^{-4}$
s-$C_4H_9N(NO_2)COOCH_3$	decane	90	$1.86 \cdot 10^{-6}$
t-$C_4H_9N(NO)COOCH_3$	CH_2Cl_2	0	10^{-2}
t-$C_4H_9N(NO_2)COOCH_3$	decane	0	$4.4 \cdot 10^{-10}$
t-$C_4H_9N(NO_2)COOCH_3$	decane	90	$7.52 \cdot 10^{-5}$
$(C_2H_5)CN(NO_2)COOCH_3$	heptane	90	$1.65 \cdot 10^{-3}$

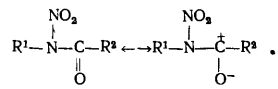
Table 13. Activation parameters for the thermal decomposition of nitrocarbamates, nitramides, and nitrosamides[71].

N-Nitro-compound	Solvent	E_a, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.
n-$C_4H_9N(NO_2)COOCH_3$	decane	34.3±0.5	−2.4
s-$C_4H_9N(NO_2)COOCH_3$	decane	30.8±0.2	−4.6
t-$C_4H_{19}N(NO_2)COOCH_3$	decane	28.8±1.2	−2.2
t-$C_4H_9N(NO_2)COOCH_3$	acetonitrile	26.2±0.2	−3.7
$(C_2H_5)_3CN(NO_2)COOCH_3$	heptane	25.9	−2
$C_2H_5N(NO_2)COC_2H_5$	heptane	27.8±1.5	−2.5
n-$C_4H_{19}N(NO)COCH_3$	xylene	29.0	—
$C_6H_5CH_2N(NO)COCH_3$	pseudocumene	28.2	—
$C_6H_5CH_2N(NO)COC(CH_3)_3$	pseudocumene	21.4	—
cyclo-$C_6H_{11}N(NO)COCH_3$	pseudocumene	23.3	—

A detailed kinetic investigation[71] of the thermal decomposition of several nitramides and nitrocarbamates was directed mainly at the influence of structure on reactivity. Decomposition followed a first-order equation, the rate presumably[71] determined by the first stage, i.e. formation of the diazoxy-ester. Tables 12 and 13 include for comparison data on related *N*-nitro-compounds. It is evident that reactivity is indeed very strongly dependent on structure. Qualitative explanations were based[71] on the view that the greater thermal stability of nitrocarbamates than of nitramides[70] was due to enhancement of the resonance stabilisation of the former by the alkoxy-group:

$$R^1{-}N(NO_2){-}C(O){-}O{-}R^2 \longleftrightarrow R^1{-}N(NO_2){-}C^+(O^-){-}O{-}R^2 \longleftrightarrow R^1{-}N(NO_2){-}C(=O^+){-}O^-{-}R^2 \cdot$$

The resonance form indicated on the extreme right is absent from nitramides:



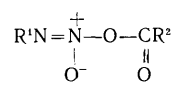
Since the transition state involves little or no resonance interaction of the alkoxy-group, the lower energy of the ground state of nitrocarbamates than of nitramides leads to a lower activation energy of decomposition of the latter.

Thermal decomposition of nitrocarbamates becomes significantly more rapid with increase in size of the substituent R^1, which may be due to non-bonding interactions of R^1 with nitro and alkoxycarbonyl groups. To a first approximation the energy of the transition state is independent of the size of R^1 (owing in particular to the near perpendicularity of the alkoxycarbonyl group to the plane of the molecule); yet as a consequence of the above non-bonding interactions the energy of the ground state is proportional to the size of R^1. As a result, increase in size lowers the activation energy of the reaction and causes "steric acceleration".

Nitramides and *N*-nitrocarbamates are thermally more stable than the corresponding *N*-nitroso-compounds. This may be partly due to greater nucleophilicity of the nitroso- than of a nitro-oxygen atom. Another explanation may be the possibility of non-bonding interaction between R^1 and a nitro-oxygen atom in the transition state. All the above factors are energetic in character, and do not affect the entropy of activation.

The above results show that nitramides and *N*-nitrocarbamates differ significantly in thermal stability, mechanism of decomposition, and dependence of reactivity on structure from the nitramines discussed previously. Since the first step in breakdown of the first two groups—formation of a diazoxy-ester—involves rupture of an $NO_2.N-CO$ bond, it must be supposed that this bond has been weakened by the carbonyl or carboxyl group. Similar weakening is absent from nitramines, so that they decompose by a different mechanism, although it must be borne in mind that Robertson's mechanism[14,26] for the decomposition of hexogen with cleavage of the ring (subsection 1) resembles the mechanism of the decomposition of nitramides and nitrocarbamates.

The mechanism of decomposition of the diazoxy-ester



is unknown. It may consist in elimination of nitrous oxide with formation of R^1 and R^2COO radicals, which then interact in the solvent cage.

8. *N*-Fluoronitramines

Graff et al.[72-74] made a series of kinetic investigations on the thermal decomposition of the isomeric *N*-fluorobutylnitramines. The first study already showed[72] that *N*-fluoro-n- and -s-butylnitramines have about the same reactivity, whereas the t-butyl compound decomposes more rapidly by a factor of 20.

A detailed kinetic investigation[73] indicated a first-order equation with parameters listed in Table 14. The course of decomposition is appreciably influenced by the nature of the solvent. Thus in ethylcyclohexane, tetrachloromethane, and a mixture of the latter with ethanol (2.5 : 1) the rate constants at 61.7 °C are (in 10^{-4} s^{-1}) respectively 14.62, 8.41, and 5.64. Table 14 shows that the activation parameters are still more strongly influenced by the nature of the solvent.

Table 14. Kinetics of the thermal decomposition of $RN(NO_2)F$ in solution[73].

T, °C	10^4k, s^{-1}	*T*, °C	10^4k, s^{-1}
R = n-C_4H_9* ($\Delta H^{\neq}=26.3\pm0.6$ kcal mole^{-1}; $\Delta S^{\neq}=0.9$ e.u.)		R=R = t-C_4H_9* ($\Delta H^{\neq}=31.6\pm1.5$ kcal mole^{-1}; $\Delta S^{\neq}=+22.7$ e.u.)	
70.1	2.13±0.10	56.2	6.53±0.20
77.2	4.37±0.26	58.6	9.72±0.97
80.8	6.15±0.20	61.3	13.63±0.60
83.3	8.53±0.40	66.1	20.00±0.28
86.4	12.08±0.42	77.3	63.33±3.3
R = s-C_4H_9* ($\Delta H^{\neq}=29.7\pm1,0$ kcal mole^{-1}; $\Delta S^{\neq}=+10,9$ e.u.)		R R = t-C_4H_9** ($\Delta H^{\neq}=22,9\pm0,4$ kcal mole^{-1}; $\Delta S^{\neq}=4,6$ e.u.)	
71.4	1.99±0.10	55.6	4.26±0.18
72.3	3.21±0.38	60.0	7.54±0.18
75.5	3.87±0.21	63.1	9.71±0.38
81.4	7.55±0.20	66.4	13.39±0.77
84.9	12.22±0.83		

*Dissolved in ethylcyclohexane.
**Dissolved in tetrachloromethane.

Table 15. Products of the thermal decomposition of *N*-fluoro-t-butylnitramine in tetrachloromethane solution[73].

Compound	*s*, %*
Nitrous oxide	5.5
Methylpropene	1.6
Acetone	5.7
2-Methyl-2-nitropropane	17.5
2-Fluoro-2-methyl-1-nitropropane	19.5
2-Methyl-1-nitropropene	5.6
2-Methyl-1-nitropropan-2-ol	24.2

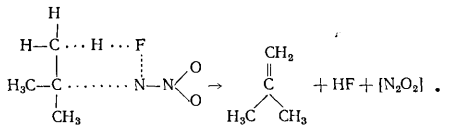
*s = relative area of chromatographic peak.

Table 15 gives the composition of the thermal decomposition products of *N*-fluoro-t-butylnitramine found chromatographically. The relative area of a chromatographic peak can be regarded to a first approximation as the proportion of the given product in the mixture. Besides the compounds listed in Table 15 hydrogen fluoride, and α-substituted isobutyraldehyde, and ammonium hexafluorosilicate were detected among the decomposition products. Nitrogen is not formed in the reaction. In special experiments on the decomposition of this nitramine labelled with nitrogen-15 in the nitro-group (5.64%) the isotope was detected in nitrous oxide (3.2%), ammonium hexafluorosilicate (4.02%), 2-fluoro-2-methyl-1-nitropropane (4.07%), and 2-methyl-1-nitropropan-2-ol (4.01%).

The complicated composition of the decomposition products led to the suggestion[73] that two mechanisms—molecular, involving a five-membered activated complex, and radical—might operate simultaneously. On the reasonable assumption that the former mechanism is characterised by a negative and

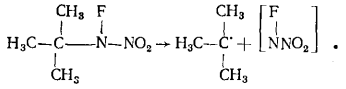
the latter by a positive entropy of activation, it may be concluded that the contributions by these mechanisms to the overall process should depend on the nature of the solvent. According to the results in Table 14 a radical mechanism predominates in ethylcyclohexane, and a molecular mechanism in tetrachloromethane.

The molecular mechanism can be represented by the scheme



It readily explains the formation of methylpropene and hydrogen fluoride, but encounters several objections. Firstly, little methylpropene is formed (Table 15), although a molecular mechanism can be expected to predominate particularly in tetrachloromethane solution. Secondly, this mechanism does not explain the formation of other decomposition products, in particular 2-methyl-2-nitropropane. Thirdly and finally, formation of nitric oxide—not nitrous oxide—must be expected from the above scheme.

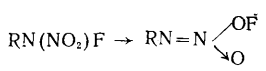
The radical mechanism was written[73]



Several special experiments were undertaken[73] to substantiate a radical mechanism. It was shown in particular that acrylonitrile readily polymerises in the presence of the isomeric *N*-fluorobutylnitramines. However, formation of the t-butyl radical could not be proved: it was not captured by the stable galvinoxyl radical; and 2,2,3,3-tetramethylbutane, which usually appears in the presence of t-butyl radicals, was not detected among the decomposition products. Finally, decomposition of the isomeric *N*-fluorobutylnitramines in toluene solution is not accompanied by formation of bibenzyl.

In the Reviewers' opinion the chief objection to a radical mechanism of decomposition lies in the low activation energies (Table 14), which do not correspond to the bond strengths in *N*-fluoronitramines: in fact the energy of dissociation of the N–F bond is close to 70 kcal mole^{-1},[72] the stability of the N–NO_2 bond has been much discussed in the preceding sections, and the C–N bond is in any case stronger than the N–N bond.

Thus the mechanism of the thermal decomposition of *N*-fluoronitramines remains in considerable measure obscure. As working hypothesis for future research it may be supposed that the mechanism is identical with that discussed in the preceding subsection for the decomposition of nitramides and nitrocarbamates. Furthermore, it would have been interesting to examine the possibility of a mechanism involving a rearrangement analogous to formation of the *aci*-form of nitro-compounds:



followed by elimination of nitrous oxide.

Analysis of the products of the thermal decomposition of *N*-fluoro-t-butylnitramine was extended to the n- and s-butyl derivatives (Tables 16 and 17).[74] Several unidentified compounds are also found in all three cases. Comparison of Tables 15–17 indicates that the n-butyl isomer on decomposition gives only n-butyl derivatives, whereas the s- and t-butyl isomers give both mono- and di-substituted butane derivatives. From this it was concluded[74] that the decomposition of the s- and t-butyl isomers, but not that of the n-butyl compound, may involve the above molecular mechanism.

Table 16. Products of the thermal decomposition of *N*-fluoro-n-butylnitramine[74].

Compound	s, %
Nitrous oxide	0.5
n-Butyl nitrate	10.3
1-Nitrobutane	16.5
n-Butyl butyrate	50.0
Butyric acid	5.9
1,1-Dinitrobutane	3.0

Table 17. Products of the thermal decomposition of *N*-fluoro-s-butylnitramine[74].

Compound	s, %
Nitrous oxide	2.3
But-1-ene	1.3
Butan-2-one	2.3
s-Butyl nitrate	2.0
2-Nitrobutane	37.0
1-Nitrobut-1-ene	9.8
2,2-Dinitrobutane	28.5

9. Primary Nitramines

Primary nitramines differ from secondary nitramines in the presence of a hydrogen atom attached to the amino-nitrogen atom: i.e. they have the general formula $RNHNO_2$. They are less thermostable than the secondary compounds, as is evident in the activation parameters of their decomposition.

The thermolysis of methylenedinitramine (medina) over the range 110–130 °C follows a first-order equation with activation energy 35.4 kcal mole^{-1} and pre-exponential factor $10^{15.6}$ s^{-1}.[75] Ethylenedinitramine (edna) also decomposes according to a first-order law, with corresponding parameters 30.5 kcal mole^{-1} and $10^{12.8}$ s^{-1} at 184–254 °C.[48]

The lower thermal stability of primary than of secondary nitramines suggests a difference in the mechanism of decomposition, most probably due to the mobile hydrogen atom of the primary nitramino-group.

Products of the thermal decomposition of medina and edna are similar in composition, consisting mainly of nitrous oxide and the corresponding aldehyde, respectively formaldehyde and acetaldehyde. Thus the thermal decomposition of edna follows essentially the stoichiometric equation[48]

$$C_2H_8N_4O_4 \rightarrow 2N_2O + CH_3CHO + H_2O.$$

It is interesting that the decomposition of primary nitramines in aqueous solution follows the same stoichiometric equation: for medina[76]

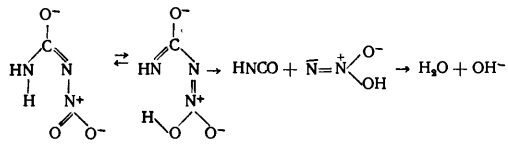
$$CH_2(NHNO_2)_2 \rightarrow 2N_2O + CH_2O + H_2O,$$

and for *N*-nitrourea[77]

$$H_2NCONHNO_2 \rightarrow HNCO + N_2O + H_2O.$$

However, ethylene glycol has also been detected[78] in the decomposition of edna in aqueous solution and in the solid phase (this paper[78] mentions that it was first detected in decomposition in aqueous solution by Franchimont and Klobbie as early as 1887).

Primary nitramines are weak acids[79], and the reactive form undergoing decomposition may correspond to the anion RN^-NO_2. Thus for nitrourea the thermolysis mechanism

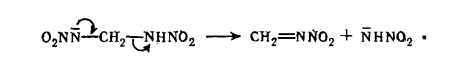


was suggested[77], with an activation energy of 27.5 kcal mole^{-1} and an activation entropy of 7.7 e.u. (pH 10). Since this compound is a nitramide, the typical mechanism (subsection 7)

$$H_2NC(O)NHNO_2 \rightarrow H_2NC(O)ON(\rightarrow O)=NH \rightarrow N_2O + H_2NCOOH \rightarrow HNCO + H_2O$$

is also possible. However, it is not altogether consistent with the kinetic results: Table 13 shows that the thermal decomposition of nitramides has negative activation entropies. Nevertheless, this mechanism cannot finally be rejected.

For the decomposition of medina in aqueous solution a mechanism has been suggested[76] analogous to the first of the above mechanisms for urea:



Subsequent processes may yield the final products:

$$CH_2=NNO_2 \rightarrow CH_2O + N_2O;\ \bar{N}HNO_2 \rightarrow N_2O + OH^-.$$

A similar scheme is in principle possible for edna:

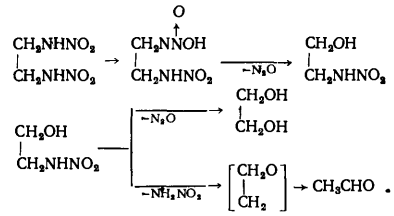
$$O_2N\bar{N}CH_2CH_2NHNO_2 \rightarrow \bar{N}HNO_2 + CH_2=CHNHNO_2;$$
$$CH_2=CHNHNO_2 \rightarrow N_2O + CH_2=CHOH;\ CH_2=CHOH \rightarrow CH_3CHO\ .$$

As primary nitramines give the same products of decomposition in the melt and in solution, identical mechanisms can be assumed. In the melt, however, the degree of ionisation is smaller and the concentration of the anionic form lower, which should tend to slow down decomposition. Primary nitramines do in fact decompose in the melt with measurable velocities at significantly higher temperatures than in aqueous solution.

In a medium of low polarity ionisation is almost completely suppressed, and a different mechanism of decomposition should operate. This apparently occurs when ring-substituted *N*-nitroanilines decompose in octan-2-ol solution[80]. Reaction takes place at a very high temperature (120 °C), nitrous oxide is not formed, and the products are nitrogen, water, the corresponding aromatic hydrocarbon, and octan-2-one. A mechanism involving intermediate formation of the *aci*-form of the nitramine and aryl radicals was suggested (RH = solvent, nitramine, or product molecule):

$$ArNHNO_2 \rightleftarrows ArN=N(\rightarrow O)OH\ ,$$
$$ArN=N(\rightarrow O)OH \rightarrow \dot{O}H + Ar\dot{N}=NO \longleftrightarrow ArN=N\dot{O}\ ,$$
$$ArN=N\dot{O} + RH \rightarrow ArN=NOH + \dot{R}\ ,$$
$$ArN=NOH \rightarrow \text{Products of ionic cleavage}\ ,$$
$$2ArN=NOH \rightarrow ArN=NON=NAr + H_2O\ ,$$
$$ArN=NON=NAr \rightarrow \dot{A}r + N_2 + ArN=N\dot{O}\ .$$

A similar mechanism, also involving formation of the *aci*-form, was suggested[78] for the thermal decomposition of edna, in order to explain the formation of both acetaldehyde and ethylene glycol:



In neutral aqueous solution edna decomposes according to a first-order equation with activation energy 32.5 kcal mole^{-1} and pre-exponential factor 10^{13} s^{-1}; increasing the acidity of the medium accelerates the reaction[76].

Kinetic study[60] of the thermal decomposition of ferrocenylmethylnitramine $FcCH_2NHNO_2$ in 2% solution at 110–130 °C shows a first-order reaction with activation energy 33.2 kcal mole^{-1} and pre-exponential factor $10^{14.98}$ s^{-1}. Decomposition of this compound thus has the same activation parameters as that of other primary nitramines, and apparently the same mechanism.

IV. DECOMPOSITION BELOW THE MELTING POINT

An important feature of the decomposition of organic explosives and in particular of nitramines at temperatures below the melting point is the formation during the reaction either of liquid products in which the initial substance dissolves or of a eutectic mixture of this compound with the products. As a consequence the process has already acquired a two-phase character soon after the start: reaction takes place in both solid and liquid phases. The quantity of liquid products increases during decomposition, and with a consequent gradual increase in the role of the liquid-phase process and decrease in that of the solid-phase process. On the other hand, the great practical experience that has now accumulated indicates that a given compound decomposes considerably more rapidly in the liquid than in the solid phase (see below). Therefore the increasing role of the liquid-phase process during decomposition should inevitably lead to autocatalysis. And indeed the autocatalytic character of decomposition below the melting point is a general feature of organic explosives, including nitramines. A formal kinetic description has been given[81,82] for such processes.

1. Tetryl

Historically tetryl was the first nitramine whose decomposition below the melting point was investigated in detail. The fact that the solid decomposes considerably more slowly than the liquid was noted as early as the 1920s.[1,2] On the basis of Lewis's ideas Hinshelwood suggested that the difference in behaviour was due merely to a difference in activation energy, in turn equal to the latent heat of fusion[2]. Simple calculation then indicates that liquid tetryl should decompose more rapidly than the solid by a factor of at least 1300, but in fact the ratio of the reaction velocities is considerably smaller at 50–100. From this Hinshelwood made the important deduction that the initial solid tetryl contained impurities (and possibly catalysts) already causing partial

occurrence of the liquid-phase reaction in the very first stages of decomposition.

Hinshelwood's calculation was based on assumptions, of course, that nowadays might be regarded as oversimplified (if only because the topochemical character of solid-phase decomposition was completely ignored). Nevertheless, his main conclusion concerning the possible role of impurities in inducing liquid-phase decomposition below the melting point seems valid. Moreover, this conclusion applies not only to tetryl but also to other solid organic compounds. Therefore the possibility of partial occurrence of the reaction in the liquid phase must always be taken into account in the investigation of decomposition below the melting point. Such possibility creates considerable difficulties in research on the decomposition of solids, for methods of monitoring small quantities of impurities and removing them from solid organic compounds have been inadequately developed.

In the above work[2] the decomposition of tetryl was studied at low degrees of conversion (when the contribution of autocatalysis by picric acid was small), in conformity with Farmer's view[1] that autocatalysis in decomposition below the melting point may be due to appearance of a eutectic mixture of tetryl with its decomposition products. Experimental results showed good agreement with calculation, despite an error in the latter[2] that has since been corrected[82].

Table 18. Activation parameters for the thermal decomposition of tetryl below the melting point.

E_a, kcal mole^{-1}	A, s^{-1}	Ref.
52.0	$10^{22.5}$	[3.53]*
36.6	$10^{12.7}$	[81]**
54.9	—	[31]

*Calculated from experimental results in Ref.1.

**In Ref.81 unpublished results are quoted that had been calculated by Wiseman from experimental data in Ref.1.

On the assumption of first order in the initial stage several calculations were made, from the initial segments of the kinetic curves, of the activation parameters of the thermal decomposition of tetryl. Table 18 shows marked discrepancies between results obtained by different authors, which may have several explanations. One lies in the above possibility of an indefinite contribution by liquid-phase decomposition to the overall process. Furthermore, as is evident from the footnotes to Table 18, in several cases the estimates were based on the few results obtained by Farmer[1], moreover within a narrow temperature range. It must also be borne in mind that the measured kinetic parameters may be influenced by the experimental conditions, in particular the extent to which the reaction vessel is filled[83,84]. As a last reason, perhaps the most important, Hall[33] found, on processing experimental results obtained by various workers on thermal decomposition both above and below the melting point, that the Arrhenius law breaks down near this temperature (more precisely for a few degrees below it): whereas at temperatures substantially below the melting point the slope of the Arrhenius relation does not greatly differ from the slope for decomposition above the melting point, so that differences in rates above and below this point are determined mainly by the pre-exponential factor, the slope increases abruptly in the immediate vicinity of the melting point, and hence the observed activation energy and pre-exponential factor increase markedly. Thus the observed activation parameters for the thermal decomposition of tetryl depend on the temperatures (relative to the melting point) at which the measurements were made. In fact breakdown of the Arrhenius law in the vicinity of the melting point is evident not only with tetryl: it is very general in character, and has been observed in the decomposition of several solids[85]. This interesting phenomenon has not yet found a rigorous explanation.

It follows from the above discussion that kinetic results for the thermal decomposition of tetryl below the melting point do not admit of a simple physical interpretation. The main details of the mechanism of the solid-phase decomposition of tetryl also remain obscure.

2. Hexogen

Decomposition at temperatures below the melting point (and also above this temperature) has been studied in greater detail for hexogen than for other nitramines. The early work on the decomposition of solid hexogen[81,35,36] already established that the kinetics follows the sigmoid law characteristic of solid-phase processes. The results that have now accumulated show that the decomposition of hexogen is extremely complicated, being subject to the influence of various factors, which of course makes interpretation of the kinetic results difficult.

The influence on decomposition of the geometry of the specimen, more precisely of the accessibility of its surface to the surrounding atmosphere, has been studied[86] in experiments with hexogen either scattered on the surface of the reaction vessel or placed in special tubes whose number was varied from one experiment to another, although the total quantity of hexogen was the same in every experiment. The construction of the tubes was modified in certain experiments, by making the outlet smaller or dividing the tube into two connecting chambers, containing the compound in its usual compact state and in an almost disperse state respectively. Change in the geometry of the specimen was found to have different effects on individual stages of the process. In any case, enhancing the accessibility of the specimen surface to the surrounding atmosphere shortens appreciably the induction period and accelerates decomposition.

It can thus be regarded as reliably established that gaseous reaction products influence the kinetics of the decomposition of hexogen. Detailed analysis of this effect led to the conclusion[86] that the gas phase contains substances that both catalyse and retard decomposition. Such compounds have been listed[35]: nitrogen dioxide in small quantities shortens the induction period, but in large quantities increases the initial rate of decomposition; nitric oxide in small quantities shortens the induction period but in large quantities lowers the initial rate; and oxygen appreciably lengthens the induction period.

Results were also obtained[35] indicating the role of reactions involving gaseous products: the process became slower as the reaction vessel was filled. The explanation was that reaction in the condensed phase was accompanied by gas-phase decomposition of partly vaporised hexogen, the role of the latter process being smaller the greater the m/V ratio. Estimates showed that, in order to explain the results, it was necessary to suppose that hexogen breaks down in the gas phase more rapidly than in the liquid by a factor of 100. This value agrees quite well with results[21] showing that the

decomposition of hexogen in the gas phase inhibited by nitric oxide takes place 10 times as rapidly as in solution; the uninhibited gas-phase reaction occurs more rapidly than in solution by factors of 30–40.

However, the arguments in Ref.35 encountered the objection[86] that with large portions of hexogen giving high m/V ratios it takes a long time to heat up the reaction vessel, and an appreciable proportion of the reaction takes place under non-isothermal conditions, which casts doubt on the correctness of the kinetic results. Thus the nature of the influence of the m/V ratio on the kinetics of the decomposition of hexogen cannot be regarded as finally elucidated. Incidentally, the above difference between rates of decomposition of hexogen in gas and liquid phases may be due to a cage effect.

Other work on the influence of gases and in particular gaseous decomposition products on the kinetics of the decomposition of hexogen[87] showed that nitrogen, carbon monoxide and dioxide, and nitrous oxide have some retarding effect; water slows down the reaction more strongly; nitric oxide, formaldehyde, and methanol accelerate the reaction; oxygen and nitrogen dioxide are inhibitors; and propene and toluene have no appreciable influence on the kinetics. A detailed study has been made of the accelerating effect of formaldehyde[88]. Yet other workers have obtained similar results[17]: nitrogen, carbon monoxide and dioxide, nitrous oxide, and water retard the reaction; nitric oxide also diminishes the rate of decomposition, but to a less extent, and formaldehyde accelerate the process.

The explanation given for the influence of nitrogen, carbon monoxide and dioxide, and nitrous oxide was that these gases prevented the vaporisation of hexogen and diminished the contribution by its gas-phase decomposition. However, when decomposition occurs in a vacuum[86], a part of the hexogen evaporates and settles on the walls of the reaction vessel: i.e. what was termed[86] a change in specimen geometry takes place. The role of this geometry was interpreted[86] as facilitation of the removal of reactive gaseous products from the surface of the specimen with increase in contact between the latter and the surrounding medium. Without objecting to this concept, we note nevertheless that a possible alternative explanation is that the role of heterogeneous reactions of gaseous products with the hexogen surface becomes greater (not smaller) with increase in such contact. It should be noted that with restricted contact between specimen and surrounding atmosphere (e.g. when the hexogen is enclosed in a narrow tube) a gaseous product formed within the specimen must first pass through it, before escaping into the atmosphere. However, the time required for such escape is brief, in any case considerably shorter than the characteristic time of the overall process of thermal decomposition.

The discrepancy in the results for the influence of nitrogen dioxide on the kinetics of the decomposition of hexogen can apparently be attributed to measurement of respectively the quantity of gas evolved[35] and the degree of conversion[87]. Since the quantity of gas evolved on the decomposition of hexogen increases in the presence of nitrogen dioxide[87], a greater quantity of gas evolved may correspond to a lower degree of conversion. Thus nitrogen dioxide apparently inhibits the decomposition of hexogen. The reasons for this phenomenon are not very clear. A possible cause is that nitrogen dioxide may be involved in two opposite processes—oxidation of the initial compound (accelerating effect) and recombination with amino-radicals arising in the primary step (inhibition)—as already discussed in connection with the gas-phase pyrolysis of nitramines[9]. The role of the latter effect on decomposition in a condensed phase may be enhanced by the cage effect. Another explanation of the inhibiting action of nitrogen dioxide is that condensed decomposition products accelerate the reaction[87], not only physically (by liquefaction) but also chemically. It is possible that nitrogen dioxide may react with the above condensed products and lower their catalytic activity. This deduction might in principle be tested by studying the influence on the thermal decomposition of hexogen exerted by condensed decomposition products previously treated with nitrogen dioxide, but such experiments have not been undertaken as far as the Reviewers are aware.

The accelerating influence of formaldehyde[86–88] may be at least partly due to its ready reduction of nitrogen dioxide to nitric oxide[89]. It is also possible that formaldehyde is able to react with hexogen itself, attacking it at a nitro-group[87].

The acceleration of the decomposition of hexogen under the influence of methanol may be closely connected with the above reactions. Methanol is able to reduce nitrogen dioxide, being oxidised to formaldehyde; furthermore, methanol may inhibit the oxidation of formaldehyde by nitrogen dioxide[87].

Nitric oxide like other gases somewhat retards decomposition by impeding evaporation[17], but it also has a chemical effect, being involved in secondary reactions and accelerating decomposition. The nature of these reactions is unknown. The view was expressed[35] that nitric oxide may yield the nitroso-analogue of hexogen, but in the absence of additional experiments this suggestion may be regarded as purely hypothetical.

An objection has appeared[86] to the above view[13–17] that hexogen undergoes slight vaporisation below the melting point with partial decomposition in the gas phase, the contribution of which to the overall process may be very considerable. All the observations could be explained[86] by the above influence (both accelerating and retarding) of gaseous decomposition products of hexogen on the kinetics of its decomposition. It was also concluded[86] that liquefaction during decomposition of solid hexogen also is unconnected with a purely gas-phase process.

Without going into the essence of the controversy, we note that there appears to be no direct disproof of either view. Moreover, we feel that these concepts are not mutually contradictory, and both gas-phase decomposition of vaporised hexogen and the influence of active gaseous products on decomposition of the solid must be accepted as possible. Greater clarity can be introduced into this question only by detailed kinetic investigation of the decomposition of hexogen solely in the gas phase and solely in the solid phase.

Several studies have been made on the important kinetic influence of crystal size on the solid-phase decomposition of hexogen. Grinding crystals of size 1–2 mm to 0.1 mm had no kinetic effect[35], and another worker[90] also found no kinetic effect of crystal size. Working with finer crystals[21] showed that at 170 °C the ground hexogen had grown to 0.003–0.01 mm after 10–20 min. Nevertheless, the ground material decomposed considerably more rapidly than a specimen with larger crystals. This can be explained both by enhanced reactivity of surface molecules of the crystal and by the above[86] influence of specimen geometry on decomposition kinetics. Thus the influence of crystal size on the kinetics of the decomposition of hexogen remains in considerable measure obscure: further research is required to clear up this problem.

Occluded solvents and gases are evolved before decomposition of hexogen begins, and therefore do not influence its course[90]. Preparation of the crystals in different ways, and also terminating the reaction by cooling the system, likewise

have no effect on the kinetics. Somewhat different results have shown[21] that acetone (the solvent from which hexogen had been recrystallised) could not be removed by drying, and its escape from the crystals during decomposition increased the observed rate of gas evolution. However, purification by sublimation combined with preliminary degasification enabled the effect of impurities of the kinetics to be eliminated. The difference between these sets of results[21,90] may be due to the different conditions—temperature, sample size, volume of reaction vessel—under which the kinetic measurements were made. The decomposition of hexogen is influenced[90] by solid additives (copper sulphate, carbazole) and also by ultraviolet irradiation.

Table 19. Activation parameters for the thermal decomposition of hexogen below the melting point.

Method	ΔT, °C	E_a, kcal mole^{-1}	A, s^{-1}	Ref.
Manometric	177—200	45.5±2.0	$10^{17.7\pm0.7}$	[81]*
Manometric	150—197	52.0	$10^{19.1}$	[35]
Manometric	170—198	43—63**	—	[91]
Manometric	170—197	44***	—	[88]
Ignition	—	52.4	—	[92]
—	—	41.5	$10^{14.5}$	[19]
Manometric	130—180	59.5	$10^{11.7}$	[20]
Manometric	140—190	40±1	—	[21]
Vibrational	22—85	(43.4—46.5)****	($10^{25.8}$—$10^{27.2}$) ****	[93]

*Unpublished results of Adams quoted in Ref.81.

**Depending on the geometry of the specimen and the segment of the kinetic curve.

***In the presence of formaldehyde.

****Depending on the experimental conditions.

Because of the complicated character of the thermal decomposition of hexogen the activation parameters (Table 19) have been calculated from the initial portions of the kinetic curves on the assumption that at low degrees of conversion reaction occurs mainly in the solid phase and is described by a first-order equation. Calorimetric data have also been published[94], but without kinetic parameters. The complexity of the process and the influence of numerous factors are especially evident in the results from Refs.88 and 91 (Table 19), according to which the activation parameters are strongly influenced by gaseous decomposition products. There is therefore every reason to suppose that the majority of the activation parameters in Table 19 are effective values characterising not a single but a whole set of reactions. The contribution by each reaction to the observed rate constant depends in general on the experimental conditions, so that the considerable scatter between the results obtained by different workers is not surprising.

Especially noteworthy are results[20,21] showing a departure from the Arrhenius law in the vicinity of the melting point, as has already been discussed in connection with tetryl. Breakdown of this law may be one reason for the high activation parameters in Table 19. Those from Refs.19—21 had been obtained over a temperature range within which the Arrhenius law applies, and if they in particular are assumed to represent the solid-phase process, it is at once evident how close are the activation energies of reactions in gas phase, solution, and solid state. This naturally suggests a common reaction mechanism, in particular that the rate-determining step in the solid phase is rupture of an $N-NO_2$ bond. The diminished pre-exponential factor from Ref.20 may be due to a cage effect or to the topochemistry of the reaction, in particular its localisation at non-equilibrium lattice defects.

Nevertheless, kinetic data alone are insufficient to prove a common mechanism of decomposition under different phase conditions, so that the alternative view of different mechanisms in gas and condensed phases[17,18] cannot be regarded as incorrect. In this connection especial attention should be paid to the concept of a definite mutual orientation of hexogen molecules in the crystal lattice, making possible bimolecular interaction between two hexogen molecules in the first stage of decomposition[37,87].

Physical aspects—the influence of crystal structure on molecular reactivity—are no less important than the above chemical aspects. As little work has been done on this problem applied to the decomposition of molecular crystals, we can welcome the use of X-ray diffraction and electron microscopy[20,95] to study physical phenomena (plastic deformation, elastic stresses) in the thermal decomposition of hexogen.

In concluding this subsection we note that research on decomposition under the influence of various physical factors—impact[96,97], electric field[98,99], vibration[100,93]—may assist understanding of the solid-phase process. Thus an electron spin resonance signal arises when hexogen is subjected to impact, which indicates the formation of free radicals during decomposition, although their nature was not revealed[96]. It was also concluded[96] that rupture of an $N-NO_2$ bond occurs in the rate-determining step. This was confirmed by later results[97], though they were based on the doubtful assumption that in hexogen a nitrogen–nitrogen bond is more stable than a carbon–nitrogen bond. The model adopted in this work[97] assumes the transfer of lattice phonons to vibrational degrees of freedom of the hexogen molecule during impact compression. Such a model provides an explanation for several observed features, in particular the slowing down of the thermal decomposition of hexogen with increase in hydrostatic pressure. It would have been interesting to develop this model to apply to the purely thermal (not impact) decomposition of nitramines.

3. Octogen

As octogen is an analogue of hexogen, its thermal decomposition exhibits similar features. This compound can exist in various polymorphic modifications[101], each with its own thermal stability, as will be shown below.

Like other solid explosives octogen decomposes autocatalytically[35,36]. The initial rate diminishes with increase in the m/V ratio[35]. As with hexogen, this effect can be attributed either to the involvement of active gaseous decomposition products or to a contribution by gas-phase pyrolysis of partly vaporised octogen to the overall reaction. The latter explanation is less probable in the case of octogen (at least in the absence of additional experiments), since it is less volatile than hexogen.

The gaseous decomposition products—nitrogen and oxides of nitrogen and carbon (Table 20)—have the usual composition for nitramines. The temperature dependence of the composition apparently indicates that these products are formed by secondary reactions. Each product is characterised by its own activation parameters, and its contribution to the overall rate depends on the temperature. Data on the isotopic composition of the decomposition products were given

in a paper[39] already mentioned in connection with liquid-phase decomposition.

Several studies have been made on the kinetic influence of crystal size. According to Maksimov[35] grinding crystals of size 1–2 mm down to 0.1 mm does not affect the initial rate of decomposition, but at the later stage of acceleration the fine crystals decompose more slowly. Visual observation showed that large crystals had retained their shape and transparency of being heated at 176 °C for 2–3 h: they began to become cloudy after 20–30 h, after the evolution of 0.5–1% of gases; but cracking began after 100–200 h (5% of gases).

Table 20. Composition of gaseous products of thermal decomposition of the β-modification of octogen (moles mole^{-1} octogen).[101]

Temp., °C	N_2O	N_2	NO	CO	CO_2	HCN	CH_2O
230	2.52	0.42	0.31	0.42	0.50	0.02	0.89
254	2.49	0.47	0.53	0.47	0.53	0.06	0.56

Table 21. Activation parameters for the thermal decomposition of octogen below the melting point.

Method (cryst. modification)	ΔT, °C	E_a, kcal mole^{-1}	A, s^{-1}	Ref.
Manometric	176–230	37.9	$10^{11.2}$	[35]
Thermal analysis (δ)	245–280	59–65*	—	[103]
DSC (α)	—	210	—	[33]
DSC (β)	—	180±15		[33]
Manometric (β)	150–170	36.0	$10^{10.8}$	[19]
		67.0	10^{25}	[20]
Manometric (α)	180–210	41.0	$10^{12.6}$	[20]
Derivatographic**	185–280	41.2	$2.2\cdot10^{14}$	[102]
Derivatographic***	160–250	27.0	$1.1\cdot10^{9}$	[102]
DSC	251–263	42±2	—	[34]
DTA	220–241	44.2–63.2 ****	—	[104]

*Depending on method of measurement.
**Crystal size 160–315 μm.
***Crystal size <50 μm.
****Depending on the temperature.

Different results have been obtained[102] by workers using finer crystal. Derivatographic investigation showed that octogen of mean crystal size 160–315 μm under non-isothermal conditions at 185–280 °C decomposes in a single stage. If, however, the octogen is ground to below 50 μm, the reaction occurs in two stages, the first of which has already begun at 160 °C. This was explained[102] in topochemical terms, by the effect of grinding in producing surface defects and dislocations possessing excess energy and hence enhanced reactivity. However, an alternative explanation is the involvement of active gaseous products, i.e. what has been termed the specimen geometry effect (subsection 2).

Table 21 shows a considerable scatter among the kinetic data obtained by different workers for the decomposition of octogen. The above complicating factors—role of gaseous decomposition products, appearance of a liquid phase during decomposition, breakdown of the Arrhenius law in the vicinity of the melting point—are partly responsible. Yet the aggregate of results reliably indicates the kinetic influence of the crystalline modification. This is supported also by the dependence of the thermal stability of octogen on its mode of recrystallisation[105] (though in this case the possible role of occluded solvent is not clear) and by vigorous decomposition of the δ-modification of octogen even at 150 °C.[106]

Despite the considerable scatter the results of several studies[19,20,34,35,102,104] show quite good mutual agreement, with activation energy ~40 kcal mole^{-1} and pre-exponential factor 10^{13} s^{-1}, values characteristic of the pyrolysis of nitramines in gas and liquid phases, which involves rupture of an N–NO_2 bond in the rate-determining stage. However, this hypothesis cannot be accepted as strictly based, and the possibility of a different mechanism for solid-phase decomposition is not excluded. In particular, the rate-determining stage in the solid-phase decomposition of octogen may be electron transfer in the crystal lattice[103,107].

The enhanced thermal stability of solid octogen in comparison with hexogen[19,20] has been explained by the greater energy of interaction between its molecules in the crystal.

In conclusion we may mention another study[94] of the thermal decomposition of octogen, but without determination of the kinetic parameters.

4. Primary Nitramines

Study of the thermal decomposition of methylenedinitramine (medina) at 70–100 °C reveals[75] a more complicated course than the sigmoid law followed by the preceding nitramines: the kinetic curve has two points of inflexion. Initially the rate of decomposition diminishes with time, after which a period of autocatalysis ensues, which is followed by fresh retardation of the reaction. At 80 °C the rate is described by the equation (t = time)

$$w = 5.5(1-e^{-0.16t}) + 0.00192t^{1.76}.$$

The results were interpreted in terms of a topochemical model[75], according to which the reaction develops on surface nuclei, whose number remains unchanged. At each centre the compound decomposes according to a first-order law until a definite quantity has changed, after which decomposition follows a power law (e.g. a second-order equation) with a significantly smaller rate constant than for the preceding first-order reaction. Analysis of this model yields an equation identical with that given above. Moreover, the model indicates that the duration of the induction period (from the start of reaction to the first point of inflexion on the kinetic curve) should depend on temperature according to the Arrhenius law, as is observed in fact with an activation energy of 27.8 kcal mole^{-1}. It was shown also that picric acid coating the crystal surface inhibits reaction, diminishing the degree of conversion during the induction period.

The chemical mechanism of the solid-phase decomposition of medina was not discussed[75], and available data are insufficient for definite conclusions to be drawn.

An undoubted merit of this work[75] is its development of a topochemical model with a complete description of the kinetic curve, which has not been done for other nitramines. However, it must be borne in mind that agreement between calculated and experimental values is not sufficient proof of the correctness of the model, since an alternative model might also agree with available experimental results. Furthermore, we do not know how far the induction period is due to impurity processes, which are extremely widespread in solid-phase decomposition.

Data on the solid-phase decomposition of ethylenedinitramine (edna) are also very sparse. As would be expected, reaction in the solid is considerably slower than in the liquid phase[48,78]. The kinetic curve resembles that for medina, with two points of inflexion; impurities and gaseous decomposition products accelerate the reaction[78]. The activation energy and the pre-exponential factor determined at 100–120 °C are respectively 36 kcal mole^{-1} and $10^{12.5}$–10^{13} s^{-1}.[78] However, this paper[78] gives results of unpublished work, according to which the activation energy depends on the temperature range, its value in a vacuum being respectively 37.0, 41.5, and 51.5 kcal mole^{-1} at 100–120, 120–135, and 135–145 °C; for atmospheric pressure the values at 120–135 and 135–145 °C were 43.5 and 59.5 kcal mole^{-1}. The pre-exponential factor remained almost unchanged over these temperature ranges at 10^{12}–10^{13} s^{-1}.

Without any grounds it is stated[78] that the decomposition of edna in a vacuum has a chain mechanism in its initial stages (2–3% conversion).

Kinetic data on the thermal decomposition of edna agree well with a first-order equation[49,30] in the initial stage (5% conversion). Between 5% and 10% a period of "autostabilisation" ensues: i.e. the observed first-order rate constant diminishes. After 10% conversion the reaction again accelerates, the rate constant increases, and a first-order equation is satisfied. The activation energy and the pre-exponential factor for the initial stage are 30.8 ± 2.0 kcal mole^{-1} and $10^{11.1 \pm 1.0}$ s^{-1}, the corresponding values in the region of "autostabilisation" being 71.7 ± 1.6 and $10^{31.6 \pm 0.8}$.[49] In view of the experimental error the values in Refs.78 and 49 show quite good agreement, and are close to those given above for the liquid-phase decomposition of primary nitramines. As in preceding cases this suggests identical reaction mechanisms in liquid and solid phases, although direct evidence for such a hypothesis is lacking.

5. Other Nitramines

Information has been published on the thermal decomposition of several other nitramines, for which kinetic parameters have not been determined. Differential thermal analysis was used to study the decomposition of nitroguanidine[28,108] and of nitramino-carboxylic acids and their salts[59]. Those of the latter that decompose below the melting point possess greater thermal stability than compounds that decompose in the liquid state. The thermal decomposition of 1,5-*endo*-methylene-3,7-dinitro-1,3,5,7-tetra-azacyclo-octane has been examined[33] by differential scanning calorimetry, and the activation energy roughly estimated as 100–300 kcal mole^{-1}.

V. CONCLUSION

It can be concluded from the above survey that considerable progress has now been made in understanding the main features of the thermal decomposition of *N*-nitro-compounds. Nevertheless, it is worth considering the unsolved problems and indicating possible routes to their solution.

In the kinetics of the gas-phase decomposition of *N*-nitro-compounds the most detailed attention has been paid to the nature of the first, rate-determining stage, although even here complete unanimity is absent, as discussed above in connection with hexogen and octogen. For the hypothesis of a radical mechanism of breakdown to be confirmed or refuted systematic investigations of the dissociation energies of bonds are necessary; these can be achieved by spectroscopic methods, thermodynamic estimates of the enthalpies of formation of nitro-compounds and free radicals, and quantum-mechanical calculations. At the same time estimation of pre-exponential factors with the help of the modern theory of unimolecular reactions will be extremely useful.

The time has arrived to pass from the first stage to a detailed analysis of the complete mechanism of the decomposition of *N*-nitro-compounds. Strange as it may seem, not even a first step has been taken in this direction: no complete quantitative analysis of the products at different stages of decomposition has been made, although standard methods of mass spectrometry and chromatography can be used for this purpose. In order to elucidate the mechanism of these reactions it is extremely important to make a kinetic study of the reactions of oxides of nitrogen, primarily of nitrogen dioxide, both with the nitramines themselves and with their decomposition products. Further, considerable interest attaches to the interaction of nitrogen dioxide with amino-radicals, mainly because this is the reverse reaction to the presumed first stage of decomposition of nitramines—rupture of an N–NO_2 bond—and its examination might reveal to what extent this first stage is reversible. Useful information on the mechanism of the thermal decomposition of *N*-nitro-compounds might be obtained from experiments on non-thermal decomposition, e.g. flash photolysis.

At the outset of research on the thermal decomposition of nitro-compounds Roginskii and Semenov put forward the hypothesis of a chain mechanism[6], but this idea was not developed. It is now considered that the decomposition is not a chain reaction, since oxides of nitrogen are formed, and these are effective inhibitors of chain processes. Clearly, however, this is not a decisive argument, and the involvement of a chain mechanism in the decomposition of nitro-compounds, including nitramines, remains an open question. Correlation analysis, enabling quantitative relations to be established between structure and reactivity, is at present widely used in organic chemistry. Unfortunately, this approach has not yet been duly applied to the pyrolysis of nitro-compounds, despite its obvious relevance. This gap must undoubtedly be bridged, for which purpose it is extremely desirable that the measurement of true rate constants of primary steps should be started and a larger number of compounds investigated to ensure statistical reliability of the results.

The problems formulated above for gas-phase pyrolysis are in urgent need of solution also for processes in the liquid phase, where moreover the use of powerful physico-chemical methods (electron spin resonance, chemical polarisation of nuclei, spin traps), permitting the study of reactive intermediates, becomes especially effective. Unfortunately, such methods, which have proved their value in the most diverse fields of chemistry, have not yet been applied to the decomposition of nitro-compounds. Incidentally, chemical polarisation of nuclei may perhaps help to reveal and study the cage effect, which has not yet been detected in the decomposition of nitro-compounds although widespread in radical liquid-phase reactions. Further investigation of the nature of catalysis and autocatalysis in the breakdown of nitro-compounds is of great practical interest, since solution of this problem is closely connected with the stabilisation of explosives. An example is tetryl, for which autocatalysis by picric acid has been reliably established, but the nature of the catalytic action is unknown.

The most urgent aspect of the solid-phase decomposition of *N*-nitro-compounds is to ascertain its topochemistry, which involves a wide range of unsolved problems: there is no proper topochemical model of the reaction (as stated above, such a model has been suggested only for medina, and then

its adequacy has not been rigorously proved); the kinetic influence of crystal size and polymorphic modification has not been ascertained; and only the first steps have been taken in studying the physical processes occurring in the crystals during decomposition (the above work by Klimenko et al.). An interesting problem in the kinetics of solid-phase decomposition is to establish the nature of the breakdown in the Arrhenius law near the melting point. The nature of the reaction centres involved in the thermal decomposition of *N*-nitro-compounds still remains unknown.

Future progress in research on the kinetics and the mechanism of the thermal decomposition of *N*-nitro-compounds will probably depend in considerable measure on the application of modern methods of investigation—field-ionisation mass spectrometry, optical spectroscopy, electron microscopy, X-ray diffraction, nuclear magnetic resonance, chemiluminescence, etc.—besides those mentioned above. The use of quantum-chemical calculations to analyse the reactivity of *N*-nitro-compounds is also promising.

It may be hoped that solution of the above problems will assist further development of the chemistry of *N*-nitro-compounds, extension of the possibilities for their practical application, and penetration of methods of chemical kinetics into the physics of combustion and explosion.

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Photonics of Organometallic Semiconductors—Copper Organoacetylides

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Processes associated with the interaction of photons with organometallic photosemiconductors are examined. Attention is concentrated on the nature of the photoelectric and optical properties of copper organoacetylides and also on the elucidation of their structures by methods using electromagnetic radiation. It is shown that the organometallic compounds can be regarded as a new class of semiconducting materials, because they have a number of properties typical for inorganic and organic semiconductors.
The bibliography contains 74 references.

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I. INTRODUCTION

The history of photoconductivity, which runs to a little more than 100 years[1], has demonstrated convincingly that each significant step forward in the study and applications of this phenomenon was associated with the appearance of new photosensitive materials with specific physicochemical properties. This was initiated by studies of elements such as germanium and silicon and subsequently inorganic compounds of the type A^3B^5, A^2B^6, and $A^2B^4C_2^5$, and vitreous, organic, and other semiconductors began to be included in the range of photosemiconducting materials. Thus the ways in which the chemical and energetic structures of newly discovered semiconducting compounds have increased in complexity can be clearly traced.

The present review deals with a new type of photosemiconductors—organometallic compounds (OMC). The wide variety of types of bonds ensured by the selection of appropriate organic ligands and metals suggests that such systems have extremely interesting physical and in particular semiconducting properties. The results of studies of the electronic processes in organometallic compounds can be used to determine the structure and energetic parameters of organometallic solids, to elucidate the mechanism of the migration of energy in them in order to find ways of achieving superconductivity in OMC at high temperatures, to model biophysical processes involving microelements in complex macromolecular systems, and to study the mechanisms of catalytic reactions proceeding via intermediate OMC. These studies are of interest also in connection with the likely usefulness of organometallic materials in various kinds of semiconductor devices in optoelectronics, in microelectronics, in the preparation of electrophotographic emulsions, for printing schemes, diapositives, microfilms, etc.

Approximately 100 organometallic compounds are now known in which an internal photoeffect has been observed and investigated. These are copper organoacetylides (COA), silver organoacetylides of the type $(M-C\equiv C-R)_x$[2-45], ferrocene[46,47], and polyconjugated polymers with double and triple bonds in the macromolecule, containing silicon, germanium, tin, and lead atoms in the conjugation chain[48]. The electronic properties and structures of these compounds are usually examined from the standpoint of ligand field theory which is understood as the set of theoretical ideas ranging from the electrostatic crystal field theory to the molecular orbital method[49-54].

Copper organoacetylides whose properties are the subject of the present review are at present the most thoroughly investigated organometallic photoconductors from the standpoint of optical and photoelectric properties. We shall consider initially the structure of copper organoacetylides on the basis of data obtained by methods involving the use of electromagnetic radiation. In considering the optical and photoelectric properties particular attention will be devoted to the relation between these two properties in the structure of copper organoacetylides, the mechanisms of the primary steps in the formation of carriers and their drift, and methods for the chemical and spectral sensitisation of the internal photoeffect in order to increase the integral photosensitivity and expand the spectral photosensitivity of copper organoacetylides. Data are presented concerning the possibility of the practical application of such compounds.

II. THE STRUCTURE OF THE COMPOUNDS

Copper organoacetylides are complex coordination polymers. The structural formulae of the monomeric units of certain copper organoacetylides, investigated in a number of studies[2-45], are presented in Table 1, which includes also the principal energetic parameters of such organoacetylides determined from the absorption and photoconductivity spectra which will be considered in this review.

The principal information about the synthesis and chemical properties of copper organoacetylides can be found in a series of communications[45,54-56]. These compounds are finely dispersed infusible and insoluble crystalline powders of different colours (from yellow to red) with resistivities

of 10^8–10^{11} Ω cm.[3,6,41] On the basis of the insolubility of the copper organoacetylides and the fact that the characteristic frequency of the triple bond in infrared spectra is reduced on average by 250 cm^{-1}, it has been suggested that copper organoacetylides are coordination polymers[57,58].

The structure of copper phenylacetylide (CPA), based on X-ray diffraction data, has been published in a monograph[49] (Fig. 1). It has the form of an infinite rectangular tube made up of copper atoms separated by specific metal–metal bond lengths and are linked to the phenylethynyl groups arranged outside the tube. Each phenylethynyl group is apparently linked by a σ-bond to one copper atom, by a symmetrical π-bond to a second copper atom, and by an asymmetric π-bond to a third copper atom. For simplicity, Fig. 1 illustrates only half of the rectangular tube. Subsequent study of the infrared spectra of a series of copper organoacetylides showed[8,16,19] that the characteristic frequency of the triple bond has been reduced to 1930–1970 cm^{-1} and depends little on the nature of the substituent in the ethynyl group of the ligand.

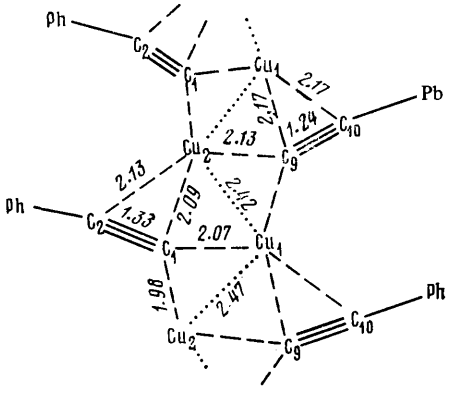


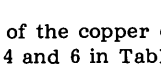
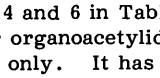
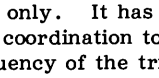
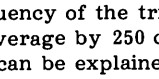
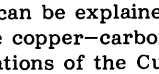
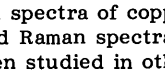
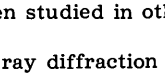
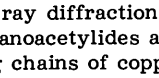
Figure 1. The structure of copper phenylacetylide $(CuC{\equiv}CPh)_x$.[49]

It follows from the infrared spectra of the copper derivatives of diacetylenic compounds (Nos. 4 and 6 in Table 1) that the copper atoms in these copper organoacetylides are coordinated to the terminal C≡C bond only. It has been suggested[16,19,20] that, apart from the coordination to the metal atoms, the decrease of the frequency of the triple bond in copper organoacetylides on average by 250 cm^{-1} compared with free organoacetylenes can be explained by the promotion of an electron along the copper–carbon bond $Cu^{\pm}C{=}C{-}R$, which leads to the vibrations of the Cu=C=C skeleton[59].

A broad asymmetric band at 130–180 cm^{-1}, which apparently reflects the presence of the copper–copper bond, has been observed in the far infrared spectra of copper organoacetylides[21]. The infrared and Raman spectra of copper organoacetylides have also been studied in other investigations[60,61].

Thus infrared spectroscopic and X-ray diffraction data make it possible to regard copper organoacetylides as coordination polymers consisting of zigzag chains of copper atoms coordinated to ethynyl groups. This structure and the quasi-allenic nature of the copper–carbon bond is confirmed by X-ray photoelectron spectroscopic data for copper organoacetylides (Table 2)[23]. The considerable shift of the $2p_{3/2}$ level of the copper atom towards higher bond energies compared with the metal indicates an effective charge transfer from the copper atom to carbon atoms of the ligands and the involvement of the *d* orbitals in the hybridisation of the Cu–C bond. The degree of charge transfer from copper atoms increases in the sequence of the compounds in Table 2. On average, the effective charge of the copper atoms in the polymers is only 0.17e when it is calculated using the Pauling electronegativities and assuming that the multiplicity of the copper–carbon bond is two. If it is assumed that the chemical shift due to the change in the effective charge by unity is 5 eV,[62] then the results indicate the transfer of an average charge of 0.4e from the copper atom. The broadening (on average by 0.5 eV) of the electronic lines in the spectra of copper organoacetylides relative to the metal apparently confirms the presence of non-equivalent copper atoms in the molecule (Fig. 1). The chemical shift ΔE_b suggests that the oxidation state of copper is close to 1.5. The shift of the 1s electronic lines of the carbon atoms in the organic ligands is, as for the level of the copper atom, in the direction of increasing binding energy compared with the free hydrocarbons but is smaller by a factor of 2. This finding indicates the conjugation of the acetylenic bonds with both copper atoms and with substituting organic groups as well as the withdrawal of electrons from these groups towards the acetylenic bond.

Table 1. The position of the long-wavelength maximum (λ) and of the optical absorption edge (*E*) and the optical activation energy for photoconduction (Δ*E*) in copper organoacetylides[34].

No.	Compound	From absorption spectra		From photoconductivity spectra	
		λ, nm	*E*, eV	λ, nm	*E*, eV
1	CuC≡C—Bu-*p*	420	2.73	440	2.72
2	CuC≡C—CH=CH_2	435	2.5	465	2.41
3	CuC≡C—CH_2—Ph	415	2.69	445	2.65
4	CuC≡C—C≡C—Ph	465	2.24	500	2.22
5	CuC≡C—Ph	465	2.45	500	2.38
6	CuC≡C—  —C≡C—Ph	475	2.3	510	2.26
7	CuC≡C—  —Ph	468	2.37	—	—
8	CuC≡C— 	467	2.30	507	2.22
9	CuC≡C— 	470	2.30	512	2.20
10	CuC≡C— 	530	2.14	550	2.14
11	CuC≡C—O—Ph	485	2.13	520	2.12
12	CuC≡C—S—Et	485	2.32	530	2.2
13	CuC≡C—S—Ph	460	2.42	530	2.08
14	CuC≡C—  —C≡CCu	512	2.10	530	2.13
15	CuC≡C—  —CCCu	470	2.00	540	2.14
16	CuC≡C—  —O——C≡CCu	550	2.00	505	2.30
17	(HC≡C—CH=CH_2+CuC≡CPh)+Cu^I	—	—	520	2.24
18	(HC≡CH+HC≡C—Ph)+Cu^I	540	1.88	620	1.92
19	(PhC≡CH+PhSH)+Cu^I	—	—	465	2.42
20	CuC≡CPBu_2	360	2.75	440	2.77
21	CuC≡CPPh_2	370	2.74	450	2.78
22	CuC≡C—$AsPh_2$	570	1.88	620	1.75

In the electron spectra of the 1s level of carbon a fine structure corresponding to different states of the carbon atoms in the ligands was not observed, although the lines are far broader than in the hydrocarbons. The observed lines are apparently due to substituents in the acetylenic groups of the ligands; otherwise one would have to expect the presence of at least two lines of identical intensity in the spectrum of copper vinylacetylide or a significant broadening of the carbon line due to chemical shifts in the different directions. It has been suggested[23] that the electron density is concentrated near the carbon atom nearest to the copper atom and that this atom in fact ensures the coordination polymeric structure of these compounds. An increase of electron density of the carbon atom nearest the metal leads to a decrease of the binding energies for all the levels of the atom, including the valence levels.

Table 2. The binding energies E_b, the electronic line half-widths $\Delta E_{1/2}$, and the chemical shifts ΔE_b (all expressed in eV) of copper organoacetylides[31].

Compound	Cu $2p_{3/2}$			C 1s		S 2p	
	E_b	$\Delta E_{1/2}$	ΔE_b	E_b	$\Delta E_{1/2}$	ΔE_b	E_b
Cu	932.2	1.8	0	—	—	—	—
CuS—Ph	933.9	2.2	1.7	286.5	3.2	1.5	163.9
CuC≡C—Ph	934.2	2.3	2.0	286.1	3.0	1.1	—
CuC≡C—C_4H_9	934.3	2.6	2.1	286.2	3.3	1.2	—
CuC≡C—CH=CH_2	934.4	2.2	2.2	286.7	3.1	1.7	—
CuO	935.1	2.3	2.9	—	—	—	—
C in hydrocarbons	—	—	—	285.0	3.0	0	—
S	—	—	—	—	—	—	164.4

The valence levels of the carbon atom nearest the copper atom apparently form a sub-band at the top of the valence band. This is also confirmed by the results of the study of the external photoeffect[31]. The photoelectric work functions for compounds with different ligands are very similar and are in the range 5.0–5.4 eV, which shows that the highest occupied state of the copper organoacetylide is determined by the structural unit Cu–C≡C. The weak but regular dependence of the photoelectric work function on the electron-donating properties of the substituent is in good qualitative agreement with the changes in the ionisation potentials of the free molecules containing the ethynyl group[63] due to the positive inductive effect of the substituents.

III. OPTICAL PROPERTIES

The optical absorption spectra of copper organoacetylides have been studied[6,8,17,20,22,33] by the diffuse reflection method[64]. The data obtained are presented in Table 1. Fig. 2 illustrates the spectra of copper organoacetylides having the general formula $(RC{\equiv}CCu)_x$. The overall characteristics obtained in the analysis of the electronic absorption spectra reduce to the following.

With increase of the conjugation chain length along the monomer unit, a bathochromic shift of the long-wave length maximum is observed. The introduction of aromatic rings leads to the appearance in the spectra of a structure due to the vibrational states. The characteristic frequencies in the absorption, photoconductivity, and photo-e.m.f. spectra can be attributed to the effect of ethynyl bonds (2100–2200 cm^{-1}), the out-of-plane deformation vibrations of the benzene ring, and the stretching vibrations of the ≡C–H group (~3200 cm^{-1}) (Table 3)[20]. The absence from the electronic absorption spectra of the 1930 cm^{-1} frequency, normally observed in the infrared spectra, suggests that in the excited state there is an alteration of the electronic configuration of the molecule, leading to an increase of the multiplicity of the ethynyl bond linked directly to the copper atom.

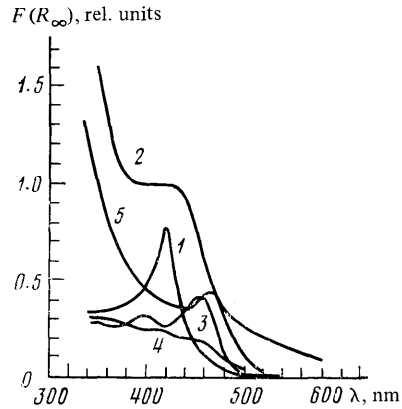
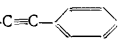
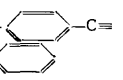


Figure 2. Optical absorption spectra of copper organoacetylides $(RC{\equiv}CCu)_x$ with different R: 1) n-Bu; 2) CH=CH_2; 3) Ph; 4) PhC≡C; 5) 1,4-C_6H_4≡CPh; $F(R_\infty)$ = Kubelka–Munk function taken from Myl'nikov[20].

Table 3. The manifestation of the vibrational structure in the absorption and photoconductivity spectra of copper organoacetylides[20].

Structural formula of monomeric unit	Positions of maxima				Frequency difference in spectra $\Delta\nu$, cm^{-1}	
	absorption spectra		photoconductivity spectra		absorption	photoconductivity
	λ, nm	ν, cm^{-1}	λ, nm	ν, cm^{-1}		
CuC≡C– 	455,395	22000, 25300	500,430	20000, 23220	3300	3220
CuC≡C–C≡C– 	455,415	2200, 24100	500,480, 450	20000, 20850, 22200	2100	850,1350 (2200)
CuC≡C–  –C≡ ≡C–	465	21500	510,490, 440	19620, 20450, 22750		830,2300 (3180)

From the standpoint of the donor–acceptor interaction, one can assume that the bands observed in the visible region are due to the resonance interaction between the *d* electrons of the copper atoms and the π electrons of the corresponding ligands[20]. Indeed acetylenic compounds of the type HC≡CR absorb in the ultraviolet, like copper(I) compounds[65]. The bathochromic shift of the absorption edge observed when the

substituent in the ethynyl group of the ligand is altered and the high absorption coefficient ($>10^4$ cm^{-1}) also confirm that the bands are due to charge transfer between the *d* orbitals of copper and the antibonding π orbitals of the ligands. Considering copper as a substituent in the main chromophore, it can be assumed that the $d-\pi$ conjugation is manifested in the spectra from the standpoint of the theory of conjugated systems and the theory of colour[20].

Analysis of the edge of the absorption band in the spectra of copper organoacetylides made it possible to determine the energies of the forward transitions[20]. For the compounds considered (the numbering is the same as in Table 1), these energies have the following values (eV): 2.75 (1) 2.53 (2) 2.48 (4), 2.50 (5), and 2.46 (6). It has also been shown that the Urbach rule holds for the edge of the absorption spectrum[20].

By altering the chemical structure, it is possible to achieve a fine control of the energetics and nature of the transitions in the COA.[17,22,33] For example, the introduction of the CH_2 group between the benzene ring and the triple bond [see compounds (3) and (5) in Table 1] interrupts the interaction with the π electrons of the benzene ring with the π electrons of the triple bond, which shifts the absorption maximum from 465 to 415 nm. Introduction of the ethynyl group instead of CH_2 [compound (4)] restores this conjugation. An increase in the number of aromatic rings in the ligand [compounds (5) and (7)–(10)] leads to a bathochromic shift of the spectra. Analysis of the spectra indicates a strong non-additive interaction of the electrons of the aromatic substituents with the intrinsic copper acetylide structural unit, which is common to all the molecules. It is known[66] that in the initial series of acenes the frequencies of the singlet–singlet transitions decrease on average by 6000 cm^{-1} following the addition of each benzene ring[66]. In the spectra of the COA with biphenylyl and naphthyl groups the long-wavelength maxima differ by only 200 cm^{-1} from the spectrum of the compound with the phenyl group, while the maximum in the spectrum of the anthracene derivative differs by 2800 cm^{-1}. The mode of addition of a further aromatic ring [compounds (7)–(9)] has little influence on the position of the long-wavelength maximum. After the introduction of substituents into the benzene ring, the bathochromic shift in the spectra increases in the following sequence: $Cl < I < OCH_3 < NO_2$.[66] The inclusion of sulphur or oxygen atoms with an unshared electron pair in the molecule increases the delocalisation of electrons along the chain. This is shown particularly strikingly when the spectra of compounds (5) and (11) are compared: evidently the introduction of an oxygen atom gives rise to a bathochromic shift of approximately 20 nm.[33]

For COA having the general formula $(R_2PC{\equiv}CCu)_x$ [compounds (20) and (21)], the nature of the absorption curves is independent of R. This fact as well as comparison of the absorption spectra of copper acetylides containing phosphino-groups with the corresponding absorption spectra of copper organoacetylides shows that the introduction of a phosphorus atom interrupts the conjugation along the monomeric unit. In contrast to phosphorus, the introduction of an arsenic atom does not affect the conjugation. Bearing in mind that the phosphorus and arsenic atoms in the tervalent state have a free electron pair which can be involved in the formation of $p-d$ donor–acceptor bonds, presumably in compounds containing such ligands there is an appreciable weakening of the $\pi-d$ bonds compared with the usual copper acetylides. The polymeric structure of these compounds is apparently due to both types of bonds.

It was noted above that the transitions in the visible region of the spectrum are due to charge transfer between the *d* orbitals of copper and the antibonding π orbitals of the ligands. At the same time an increase of absorption on passing to the short-wavelength region is a striking feature of almost all the COA. One should also bear in mind that the power relation between the absorption coefficient and the photon energy above the optical absorption edge has been obtained[20] with a power exponent of 1/2, which is characteristic of forward dipole-allowed transitions; all these features suggest that the charge transfer bands in the long-wavelength region of the absorption spectra are superimposed on transitions of the band–band type. The absorption of light is determined by transitions of the band–band type and by charge transfer between the copper atoms and the ligands.

IV. PHOTOELECTRIC PROPERTIES

The photoelectric properties of the COA have been studied in fair detail[3–10,12–19,22,24,25,27–34,39–45] by the photoconductimetric and photo-e.m.f. methods. The resistance of the specimens decreases from 10^7–10^{11} Ω to 10^5–10^7 Ω under the influence of monochromatic light with an intensity of 10^{13} photons cm^{-2} s^{-1}. The maximum photocurrents reach 10^{-5} A.[6]

The dependence of the photocurrent i_{ph} on the degree of illumination *L* is expressed by the formula $i_{ph}=\alpha L^n$, where $0.5<n<1$.[3,6,32,33,41] It has been shown that the COA exhibit a predominantly *p*-type conductivity[3,6,40]. Ohm's law holds for the dark photocurrent only for electric field strengths up to 10^2 V cm^{-1}, after which the current increases faster than the potential, which is apparently associated with space charge. The study of the relaxation of photoconductivity has shown[6,33] that a steady photocurrent is established as a rule after 1–2 min. For the majority of compounds, the descent of the kinetic curves obeys a hyperbolic relation. Specimens with an extremely high degree of inertia, in which the relaxation phenomena take place over a period of several hours, are also encountered [compounds (7) and (22), Table 1].[33]

Prolonged relaxation processes in COA, apparently due to the large number of inhomogeneities and in some cases also photochemical phenomena, are in essence analogues of the memory effects widely investigated in inorganic photosemiconductors[67]. The most reasonable explanation of the prolonged relaxations of photoconductivity in semiconductors is provided by the barrier model[67], which postulates the presence in the specimen of collective (microscopic) potential barriers.

There exist extensive experimental data on the photoconductivity and photo-e.m.f. spectra of copper organoacetylides with various substituents in the ethynyl group of the ligand[3,6,9,14,17,19,22,33,40,41]. The photoconductivity spectra of compounds of the type $(RC{\equiv}CCu)_x$ are presented in Fig. 3[19]. Analysis of the photoconductivity spectra of the COA shows that they exhibit the principal features typical of the absorption spectra of the COA, namely (1) there is a bathochromic shift with increase in the number of electrons in the substituent of the ethynyl group and there is a simultaneous decrease of the optical activation energy for photoconduction (Table 1), (2) the structure of the spectra is determined by the vibrational states, and (3) the bands are due to charge transfer between the Cu atoms and the C≡C bond with manifestation of $d-\pi$ conjugation.

In most compounds photoconductivity is accompanied by a photo-e.m.f.[3,6,8,16,19,22,23,33]. The most common result is a hypsochromic shift of the photo-e.m.f. spectra relative to

the photoconductivity spectra (Fig. 4); the maxima of the photoconductivity spectra then coincide with the minima of the photo-e.m.f. spectra. The optical activation energies for photosensitivity, determined from the photoconductivity and photo-e.m.f. spectra, agree with one another and with the energy of the edge in the optical absorption spectra. Analysis of the photoconductivity and photo-e.m.f. spectra from the standpoint of the influence of the chemical structure of the molecule has been carried out for COA with aliphatic and aromatic substituents[3,6,8,16,17,22,41] and with heteroatoms[15,17,33] in the ligand. Mixed acetylides [compounds (17) and (18) in Table 1] have been investigated together with individual acetylides[16,19].

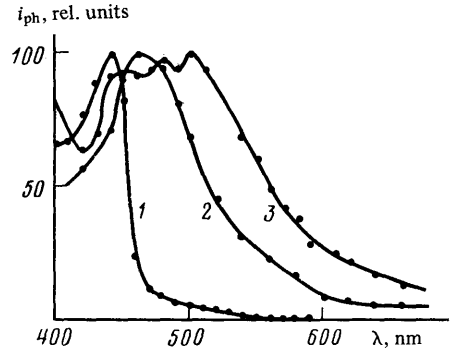


Figure 3. Photoconductivity spectra of the compounds $(RC{\equiv}CCu)_x$ with different R: 1) n-Bu; 2) $CH{=}CH_2$; 3) $PhC{\equiv}C$.[19]

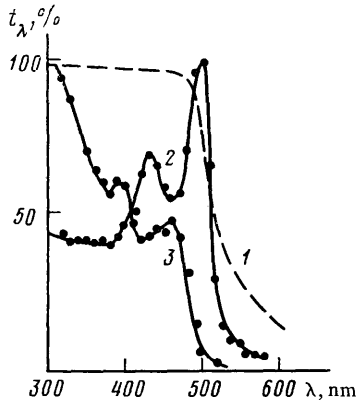


Figure 4. Absorption (curve *1*), photoconductivity (curve *2*), and photo-e.m.f. (curve *3*) spectra of copper phenylacetylide[3]; t_λ = transmittance.

A study has been made[32] of the photoconductivities of certain COA which occur under the influence of powerful laser radiation. The lux–ampere characteristic of the impurity photoconductivities is close to the characteristic obtained under illumination in the region of the fundamental absorption. This shows that the laser pulse probes the local levels directly. The optical stability of the COA decreases monotonically with decrease of the energy of the optical absorption edge.

V. RELATION BETWEEN THE OPTICAL AND PHOTOELECTRIC PROPERTIES

In order to understand the nature of the photoelectric processes, it is of interest to compare the photoconductivity and absorption spectra[3,6,17,20,22,33]. Such a comparison has been carried out in Figs. 5, 6, and 7 for COA with different substituents in the ligand. It was shown above (Table 1) that there is a fairly satisfactory correspondence between the optical activation energy for the photoeffect and the energy of the optical absorption edge.

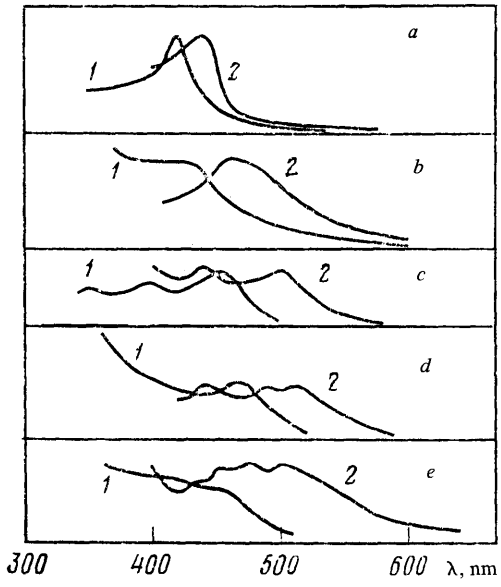


Figure 5. Absorption (curves *1*) and photoconductivity (curves *2*) spectra of copper organoacetylides[19,20]: *a*) $(CuC{\equiv}C{-}C_4H_9)_x$; *b*) $(CuC{\equiv}C{-}CH{-}CH_2)_x$; *c*) $(CuC{\equiv}CPh)_x$; *d*) $(CuC{\equiv}C{-}Ph{-}C{\equiv}C{-}Ph)_x$; *e*) $(CuC{\equiv}C{-}C{\equiv}C{-}Ph)_x$.

The principal photoconductivity maximum is as a rule located on the descending branch of the fundamental absorption. This relation between the absorption and photoconductivity spectra is as a rule fairly general in photosemiconductors and can be accounted for by the decrease in the life-time of the photocurrent carriers in the region of strong absorption due to the increased rate of surface recombination[68,69]. It is noteworthy that the low photosensitivity ("tail") in the majority of compounds investigated persists up to 1000 nm. This phenomenon is probably related to the lack of order and different sizes of the coordination blocks.

It was noted above that the absorption and photoeffect spectral bands, due to charge transfer between the ligand and the metal, are apparently superimposed on transitions of the band–band type. Bearing in mind the complex

structure of the spectra, it is difficult to determine unambiguously which types of transition are most effective in the formation of free carriers. The molecular nature (vibronic structure) of the photoconductivity, photo-e.m.f., absorption, and luminescence spectra is one of the indications that, as for organic semiconductors, a molecular excited state of the type of the Frenkel' exciton is involved in the primary step of the internal photoeffect in COA, migrating in the macromolecule until it encounters a defect or another exciton, which results in the formation of free charge carriers. On the other hand, it has been shown[42,43] that the temperature dependence of the photoconductivity of copper phenylacetylide at a frequency of 10^{10} Hz is insignificant, which can indicate either that the exciton decomposition energy is low or that band–band transitions are involved in the generation of carriers.

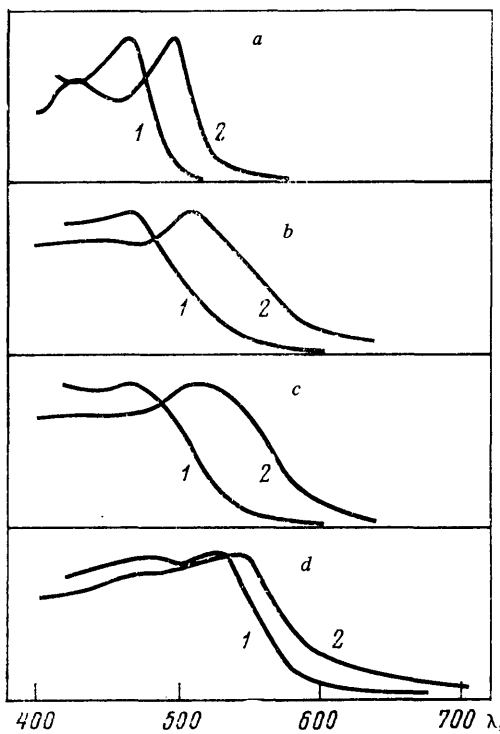


Figure 6. Absorption (curves *1*) and photoconductivity (curves *2*) spectra of copper organoacetylides with organic substituents in the ligand[22]: *a*) $(CuC{\equiv}C{-}Ph)_x$; *b*) $\left(CuC{\equiv}C{-}\text{C}_{10}\text{H}_7\right)_x$; *c*) $\left(CuC{\equiv}C{-}\text{C}_{14}\text{H}_9\right)_x$; *d*) $\left(CuC{\equiv}C{-}\text{C}_{14}\text{H}_9\right)_x$.

A direct determination of mobility in copper phenylacetylide yielded 0.10–0.05 $cm^2\ V^{-1}\ s^{-1}$ for holes and 0.18–0.05 $cm^2\ V^{-1}\ s^{-1}$ for electrons. Such mobilities show that the solid state bands in COA are extremely narrow and one must consider a jump mechanism of the movement of carriers in COA. It has been shown[70] that the mobility in copper phenylacetylide depends on temperature with an activation energy of 0.2 eV and that five adhesion levels are located in the valence band in the range of energies 0.07–0.1 eV and are combined into a narrow band with a width of 3×10^{-1} eV. The above facts suggest that the mechanism of conduction in COA reduces to a series of consecutive thermally activated jumps involving adhesion levels.

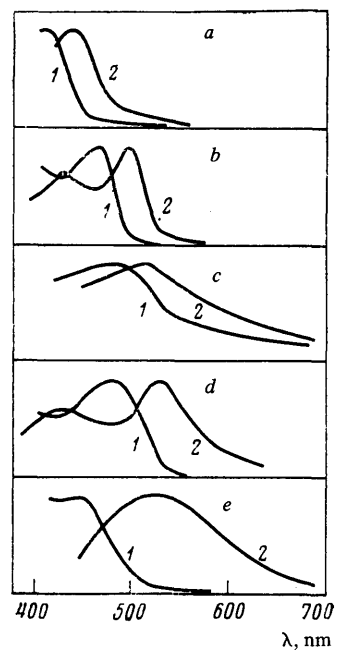


Figure 7. Absorption (curves *1*) and photoconductivity (curves *2*) spectra of organoelemental copper acetylides[33]: *a*) $\left(CuC{\equiv}C{-}CH_2{-}\text{C}_6\text{H}_5\right)_x$; *b*) $\left(CuC{\equiv}C{-}\text{C}_6\text{H}_5\right)_x$; *c*) $\left(CuC{\equiv}C{-}O{-}\text{C}_6\text{H}_5\right)_x$; *d*) $(CuC{\equiv}C{-}S{-}C_2H_5)_x$; *e*) $\left(CuC{\equiv}C{-}S{-}\text{C}_6\text{H}_5\right)_x$.

Spectroscopic studies make it possible to discover the influence of molecular structure on optical and photoelectric properties. It has been shown[2,13] that COA exhibit a much greater photoelectric sensitivity than polymers with triple bonds but without metal atoms. This shows that the coordinating copper atoms and the ethynyl groups play an important role in ensuring photosensitivity. Together with these, steric factors, which are determined by the size of the ligands as well as the size of the main chain, are decisive for charge transfer. Thus photosensitivity diminishes in the series of copper phenyl-, naphthyl-, and anthryl-acetylides [compounds (5), (8), (9) and (10) in Table 1][22,41]. The same type of relation has been established for compounds with heterocyclic substituents in the ligand[17,33]. Thus, despite the increase of the number of π electrons and of the degree of their delocalisation, the photosensitivity falls. Since the efficiency of light absorption and hence of the

formation of carriers apparently varies little, one must suppose that the decrease of photosensitivity is caused mainly by the fact that drift is difficult owing to the bulky nature of the substituents.

For aromatic substituents, the size of the ligands is fairly large but the latter ensure close packing, probably due to their planar structure, which facilitates charge transfer. In this case one may expect that, in compounds with non-planar bulky substituents, the photosensitivity should be a minimum. This has been confirmed by the finding that no photosensitivity has been observed in $(RC{\equiv}CCu)_x$ with R = t-butyl, ferrocenyl, and *o*-carboranyl[33].

Summarising, one may conclude that the decisive factor for charge transfer in COA is not the length of the conjugation system but intramolecular and intermolecular configuration interactions (short-range order in the terminology of the orthodox semiconductor physics), which lower the potential barriers at the boundaries between the macromolecules.

Apart from copper acetylides, we are aware of only one organometallic compound (ferrocene) whose photoconductivity spectrum has been measured[47]. The photocurrent increased monotonically in the range from 270 to 230 nm and no photoconductivity was observed in the regions with a low oscillator strength (320 and 440 nm). According to Hoestery and Letson[47], the latter can be explained either by the inadequacy of the energies of two excitons for the formation of carriers or by the fact that the life time of excitons is too short and the rate of their migration is too low to ensure a high probability of their annihilation. Bearing in mind the narrowness of the section of the spectrum in which the photocurrent was measured, one should apparently exercise extreme caution in stating that the photoconductivity spectrum is identical with the absorption spectrum in the region of the $\pi-\pi^*$ transitions. We may note that the mobility of holes in a ferrocene single crystal was determined in the same investigation as 2.2×10^{-2} cm^2 V^{-1} s^{-1} at 300 K and a number of considerations concerning the conduction mechanism were put forward.

VI. THE PHOTOEFFECT AND LUMINESCENCE

The absorption of light leads to the excitation of the macromolecule. Radiationless degradation of energy, luminescence, and the formation of free carriers are the possible ways in which the excited states are deactivated. We shall therefore consider studies[6,8,9] in which the luminescence and photoelectric properties of copper phenylacetylide (CPA) were investigated simultaneously. Fig.8 presents the absorption, photo-e.m.f., and luminescence spectra of CPA. The luminescence yield varies linearly with the excitation intensity in the range 313–436 nm, is insensitive to the presence or absence of air, and has two maxima, at 516 and 583 nm. Preliminary irradiation of CPA with ultraviolet light decreases the integral luminescence yield and simultaneously increases the integral photoeffect[8]. This is manifested spectroscopically (Fig.9) by a redistribution of the maxima in the action spectra, which is most strikingly manifested in the luminescence spectra. Preliminary irradiation *in vacuo* is accompanied by more complex changes in the photo-e.m.f. spectrum[4]. The luminescence is determined by the decay of excitons.

The changes in the spectra on irradiation with ultraviolet light are probably caused by the photolysis of the coordinate bonds in the polymer, which results in a change of the ratio of the polymer-homologues of the substance. When bonds are broken, the decomposition of excitons by defects is facilitated, which increases the photoeffect and diminishes the luminescence yield.

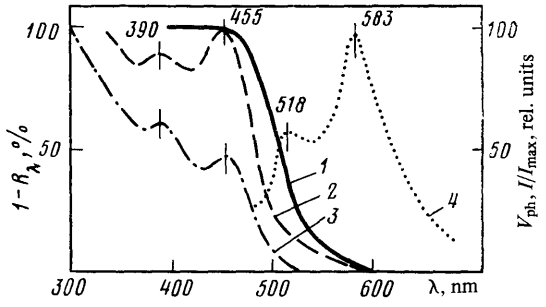


Figure 8. Spectroscopic data for copper phenylacetylide; 1) distribution of reflections ($1-R_\lambda$) from CPA in powder form; 2) distribution of reflections ($1-R_\lambda$) from CPA "diluted" with magnesium oxide (1:100); 3) photo-e.m.f.; 4) luminescence at $T = 293$ K.[8]

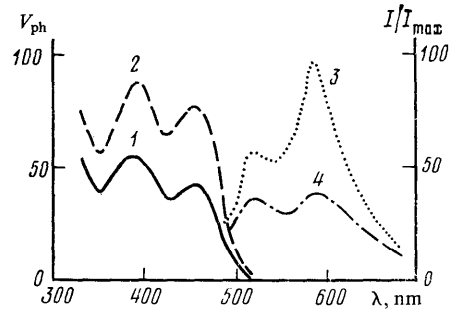


Figure 9. Variation of the luminescence intensity and photo-e.m.f. on irradiation of copper phenylacetylide with ultraviolet light: 1) photo-e.m.f. of the initial specimen; 2) ditto after 10 min irradiation with the light from an SVD-120 lamp using a water filter; 3) luminescence of the initial specimen; 4) ditto after 10 min irradiation with the light from an SVD-120 lamp using a water filter according to the data of Lashkov and Myl'nikov[8].

The proposed mechanism has been confirmed by low-temperature luminescence experiments[8] in which it was shown by spectroscopic studies that the degradation of CPA by ultraviolet light takes place as far as the formation of individual diphenylbutadiyne molecules implanted in the polymer structure. It is of interest that the phosphorescence of the diphenylbutadiyne molecules adsorbed on CPA (their absorption band is located at wavelengths below 340 nm) is excited by light at a wavelength of 365 nm. One can therefore postulate energy transfer from the semiconductor support to the diphenylbutadiyne molecules adsorbed on it. The low-temperature experiment showed that the luminescence of CPA is associated with radiative transitions on the surface. It was found that the state of the surface has a significant influence also on the photoelectric properties of organometallic photosemiconductors.

VII. THE INFLUENCE OF VAPOURS AND GASES ON THE SEMICONDUCTING PROPERTIES OF COA

The influence of oxygen, water vapour, mercury vapour, and electron-accepting molecules on the electrical conductivity, photoconductivity, and photo-e.m.f. of copper phenylacetylide has been studied in a number of investigations[4-9,14,41]. The nature of the change in the electrical conductivity and photoconductivity of CPA under the influence of oxygen is illustrated in Fig.10. The absence of a photochemical interaction of CPA with oxygen was demonstrated, since the spectral characteristics of the photosensitivity hardly changed.

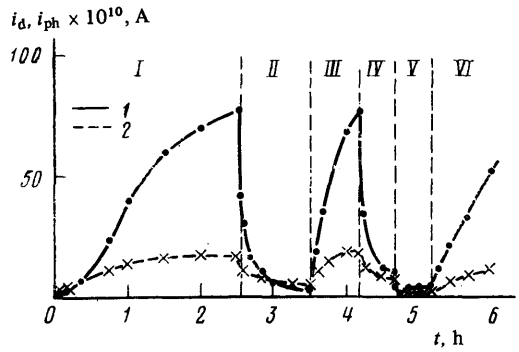


Figure 10. The influence of oxygen on the electrical conductivity (curve *1*) and photoconductivity (curve *2*) of CPA: I) evacuation of air to 5×10^{-5} mmHg; II) admission of oxygen; III) evacuation; IV) admission of oxygen; V) discharge in oxygen; VI) evacuation[4].

It is known that the adsorption of gases on the surface of the semiconductor can lead to the formation of a double layer due to adsorbed molecules or of new recombination or adhesion centres. For a *p*-type semiconductor, it has come to be assumed that the adsorption of molecules with an electron affinity should increase the photoconductivity owing to the capture of an electron by the adsorbed molecule. CPA, a *p*-type semiconductor, shows the opposite behaviour. Oxygen apparently generates new effective recombination centres, which decrease the lifetime of the majority carriers (holes); this has been demonstrated particularly by the present author[4]. On the basis of the analysis of the effect of oxygen, water vapour, and preliminary ultraviolet irradiation on the photo-e.m.f. and photoconductivity spectra, it was postulated in the same study that *in vacuo* oxygen undergoes effective photodesorption from the CPA surface. The suppression of the electrical conductivity and photoconductivity of eleven copper organoacetylides *in vacuo* compared with dry air has been demonstrated[41].

It has been shown[6,7] that water vapour suppresses reversibly the electrical conductivity and photoconductivity and increases the photo-e.m.f. of CPA, which is caused by the formation of an electrical double layer owing to surface states which capture the majority carriers. The change in the semiconducting properties of polymers under the influence of electron-accepting (quinone, chloranil) molecules is associated with the capture of conductivity electrons by these molecules. The set of results obtained concerning the influence of vapours and gases on the semiconducting properties confirms the significant role of the surface for the understanding of the photoelectric processes in organometallic compounds.

In this connection we may note that CPA proved to be a catalyst[11] of the oxidation of the leuco-form of thionine by atmospheric oxygen. The reaction is of interest, since many catalytic reactions on metals proceed via the formation of intermediate organometallic compounds.

VIII. THE SENSITISATION OF THE INTERNAL PHOTOEFFECT

The results considered above suggest that COA constitute a new class of substances with photoelectric properties. However, in many instances the photoelectric sensitivity of these materials is low or is observed at shorter wavelengths in the spectrum than are required for practical applications. All these factors give rise to the question of ways of expanding the spectral sensitivity and of increasing the integral photosensitivity of these compounds.

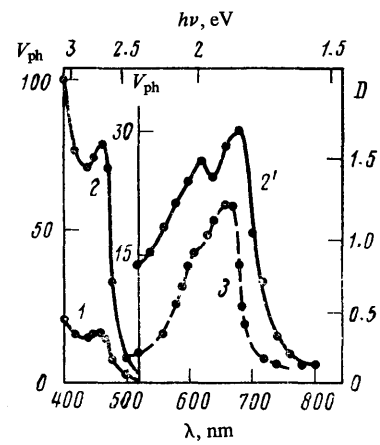


Figure 11. Spectral distribution of the photo-e.m.f. of copper phenylacetylide: 1) before dyeing; 2) and 2') after dyeing in solution of Methylene Blue; 3) absorption spectrum of 10^{-3} M solution of Methylene Blue in ethanol (D = optical density)[25].

A powerful means of increasing the photoelectric sensitivity of inorganic semiconductors is known to be chemical and spectral sensitisation[71]. Chemical sensitisation can be usefully defined as different kinds of treatment of the semiconductor leading to an increase of the photoelectric sensitivity without an alteration of the spectral characteristics of the material. The effect of spectral sensitisation consists in the manifestation of photoelectric sensitivity in the absorption band of molecules adsorbed on the surface of the semiconductor or injected into the latter. For COA, the spectral sensitisation of the internal photoeffect was first observed in studies[24,25] of the adsorption of dyes on the surface of CPA. Subsequently a number of studies of the principal characteristics of the spectral sensitisation of

copper organoacetylides were carried out[24-30,34]. The sensitisation of the photoconductivity and the photo-e.m.f. has been observed in the visible and near infrared regions of the spectrum using dyes of different classes: cationic (pinacyanol, Methylene Blue, carbocyanines, and pentacyanines), anionic (erythrosine), and non-ionic (chlorophyll, phthalocyanine, and haematin). Typical results for the sensitisation of the photo-e.m.f. and the photoconductivity of CPA are presented in Fig.11 in relation to Methylene Blue.

Analysis of the above studies[24-30,34] has led to the following findings. The sensitised photosensitivity spectrum is close to the absorption spectrum of the dye in solution. The increase in the intensity of the bands in the regions corresponding to dimeric and more highly aggregated forms of the dye in the photosensitivity spectra compared with the absorption spectra of the solutions of the dyes leads to the conclusion that, apart from the molecularly dispersed form of the dye, its more highly aggregated forms are involved in the sensitisation step.

The study of the efficiency of sensitisation as a function of the dye concentration showed that the sensitised photosensitivity reaches 30–40% of the intrinsic sensitivity. A dye concentration in solution of 10^{-3} M proved to be the most effective for spectral sensitisation. With increase of the dye concentration from 10^{-6} to 10^{-2} M, an increase in the intensity of the bands due to the dimeric and more highly aggregated forms has been observed in the sensitisation spectra. The sign of the carriers (positive) in the region of intrinsic photosensitivity of the polymeric photosemiconductor and in the region of sensitisation is as a rule the same. Instances of a change in the polarity of the sensitised photo-e.m.f. relative to the polarity of the intrinsic photo-e.m.f. have also been observed. The nature of such changes in sign as a function of time apparently reflects the kinetics of the adsorption of the dye on the COA surface[25].

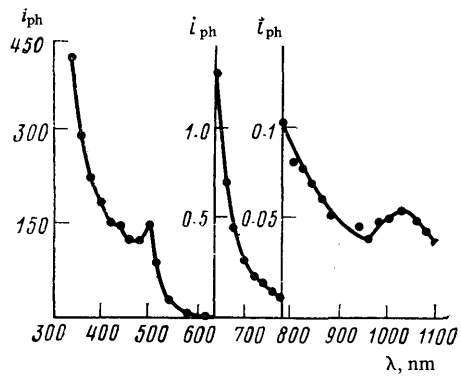


Figure 12. The photoconductivity spectrum of copper phenylacetylide dyed with pentacarbocyanine[26].

Systems based on organic semiconductors with photosensitivity in the near infrared are of considerable interest for technical purposes. The sensitisation of the COA photoeffect by pentacarbocyanine (Fig.12), allocyanine, and xenocyanine, which ensure photosensitivity up to 1300 nm, has been observed[26,28,29]. The principal features of the infrared sensitisers are analogous to those observed in sensitisation in the visible region of the spectrum.

It is noteworthy that, apart from the appearance of sensitised photosensitivity, the adsorption of dyes alters the absolute magnitude of the photoeffect in the region of the intrinsic absorption of the COA. For example, the adsorption of erythrosine increases the intrinsic photo-e.m.f. of CPA by a factor of 30.[24] The effect is apparently due to the type of traps generated by the adsorbate. This has been confirmed particularly by the increase of the inertia of the photoconductivity of coloured compounds relative to non-coloured compounds[28,29].

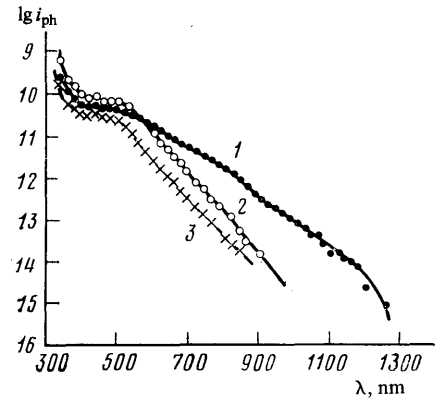


Figure 13. The photoconductivity spectrum of copper phenylacetylide dyed with polyoxyphenylene in solutions at different concentrations (g cm^{-3}): 1) 10^{-1}; 2) 10^{-2}; 3) 10^{-3}.[30]

As already stated, the use of organic dyes as sensitisers leads to the appearance of photosensitivity, whose spectral characteristics are determined by the absorption spectrum of the dye in solution. The majority of dyes have fairly narrow absorption bands, which makes it impossible to obtain panchromatic sensitivity in wide spectral ranges. In 1968 it was suggested for the first time[72] that organic polymers with conjugated bonds, characterised by diffuse structureless absorption spectra, be used as high-resistance photosemiconductors. Together with panchromatic sensitivity within wide spectral ranges, such polymer sensitisers also exhibit a high thermal stability. In addition, in selecting the appropriate polymer sensitiser, one can in principle do without non-photoactive polymeric binders in preparing electrophotographic layers.

Polyphenylenes and polyoxyphenylenes have been used[27,29,30] as sensitisers of COA. Typical curves for the polyoxyphenylene-sensitised photoconductivity of CPA at different sensitiser concentrations are presented in Fig.13. The principal characteristics of the sensitisation by polymers proved to be the same as those for dyes. In particular, the optimum sensitisation was observed for polymer concentrations in the range 10^{-1}–10^{-2} g cm^{-3} and the intrinsic photosensitivity of the adsorbent also changed following the adsorption of the polymer sensitisers.

It is noteworthy that a significant difference in the spectral distribution of the sensitiser efficiency has not been observed for polymers with different numbers of monomeric units in the sensitiser macromolecule. This may be associated with the fact that polyconjugation does not extend over the entire length of the polymer chain[30]. There is no doubt that the use of organic polymers as sensitisers will make it possible to increase significantly the integral sensitivity and to expand the spectral sensitivity of photosemiconductor devices (in particular electrophotographic layers) based on high-resistance photosemiconductors. It is to be expected that the use of polymers as sensitisers of photographic emulsions will also prove to be extremely effective.

In considering problems associated with the sensitisation of the photo-effect by organic polymers, one should note that the organometallic compounds themselves can behave as sensitisers when they are introduced into polymer matrices. It has been suggested[18] that CPA introduced into polyvinylcarbazole at the *N*-vinylcarbazole polymerisation stage acts as a sensitiser.

The above study[18] was carried out because the system comprising polyvinylcarbazole and CPA proved to be effective as electrophotographic layers[35,36,48]. In particular, it was shown that such layers exhibit a photosensitivity comparable to the sensitivity of the electrophotographic layers based on zinc oxide and selenium[40]. It was suggested that a complex involving charge transfer between the components is then formed. However, the photoconductivity spectrum of the system virtually coincides with that of CPA, while the sensitivity of the system in the visible region is higher than that of the pure CPA. Thus one can assume that a charge-transfer complex is not formed in such a system or is too weak to be manifested spectroscopically. Apparently, when light is absorbed, the formation of intrinsic carriers in CPA is accompanied by the effective transfer of part of the light energy to polyvinylcarbazole, which generates electron–hole pairs. Presumably the drift of the carriers (holes) in such a system takes place via jump photoconduction[18].

The main problem of the mechanism of spectral sensitisation is known to consist in the fact that, under the influence of a photon whose energy is significantly smaller than the width of the forbidden gap of the semiconductor, the charge carrier appears in the conductivity band. The majority of modern theories deal with alternative mechanisms of the transfer of energy of an electron from an adsorbed sensitiser to a semiconductor[71]. It is noteworthy that the problem of the mechanism of spectral sensitisation has not been finally solved even for inorganic semiconductors.

Analysis of studies[24–30,34] on the sensitisation of the COA photoeffect has shown that its principal features are the same as those observed for inorganic photosemiconductors (zinc oxide, silver halides). This suggests that the sensitisation has identical mechanisms in the two instances.

A critical examination of the existing views suggests that the preferred mechanism of spectral sensitisation involves energy transfer from the adsorbate to the adsorbent. The most significant evidence in support of this is the relative positions of the energy levels of the COA and the sensitiser dyes[34]. It is seen from the example presented in Fig. 14 that the levels of the sensitiser dyes can be located both above (pinacyanol, chlorophyll, and cryptocyanine) and below (erythrosine and Methylene Blue) the ground state of CPA. Furthermore, for the transfer of a hole to a *p*-type semiconductor it is necessary that the singlet ground level of the dye should be located below the top of the filled semiconductor band. For infrared sensitisers, even a correction for the adsorbed state cannot ensure an arrangement of levels necessary for the transfer of a hole. The relative positions of the energy levels of the COA and the sensitiser are thus not decisive for the sensitisation effect.

In previous sections it was stated that water and mercury vapours, the addition of electron-accepting oxygen compounds, as well as the adsorption of dyes and organic polymers on the surfaces of the COA lead to an alteration of the intrinsic photoelectric sensitivity of the latter. All these phenomena can be regarded as the manifestation of the chemical sensitisation of the internal photoeffect in organometallic semiconductors.

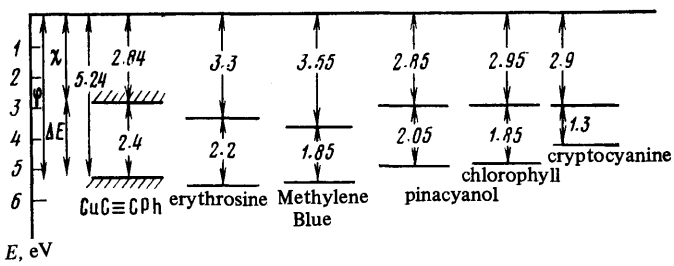


Figure 14. Schematic illustration of the energy levels of copper phenylacetylide and sensitiser dyes; ϕ = photoelectric work function; ΔE = energy of the optical absorption edge; χ = electron affinity[34].

We may also note a study[12] in which it was shown that the photoconductivity, the photo-e.m.f., and the electrical conductivity of CPA increase by 2–3 orders of magnitude when the specimen is treated with deoxyribonucleic (DNA) and ribonucleic (RNA) acids. The nature of the photosensitivity spectra does not then change significantly. The use of pyrimidine (thymine, cytosine, and uracil) and purine (adenine and guanine) bases, which form part of the composition of the acids, shows that the same effects are observed only for adenine and are somewhat smaller in the case of thymine. It is remarkable that these bases are paired in DNA. The observed effects have been explained[12] in terms of a model where the increase of the photosensitivity of the CPA is considered to be a consequence of the introduction into the latter of new recombination centres involving adenine, which increase the lifetime of the majority carriers, this being confirmed particularly by kinetic measurements. Such a model has been considered, for example, in the sensitisation of the photoeffect in cadmium sulphide[73].

We may note that the method of investigating the chemical sensitisation by biologically active molecules in specially sensitised model systems is apparently promising for the understanding of specific properties of such molecules.

IX. THE APPLICATIONS OF ORGANOMETALLIC PHOTOSEMICONDUCTORS

The discovery and study of the photoelectric sensitivity in organometallic compounds leads to the possibility of using them in many technical devices where the main photosensitive element is made of these materials. In this connection we may point out that COA and polyacetylenes containing germanium, silicon, tin, and lead atoms in the conjugation chain have been suggested as electrophotographic layers[10, 35–40,45,48]. The photosensitivity under electrophotographic conditions, determined from the decrease of the potential by

a factor of two, amounts to 300 lux s for CPA in polyvinylbutyral and 70 lux s in polyvinylcarbazole. Thus layers with COA have an integral sensitivity comparable to those of layers made of amorphous selenium and paper containing zinc oxide[10,39,40].

We may note that studies under electrophotographic conditions[10,40] confirmed the nature of the spectral distribution of the internal photoeffect, the sign of the charge carrier, and the activation of the photosensitivity of COA by preliminary ultraviolet irradiation, which was demonstrated by the photoconductimetric and photo-e.m.f. methods[3-6]. At the same time electrophotographic methods made it possible to obtain a series of new data concerning the mechanism of photoconduction in organometallic compounds.

The procedure for the preparation of transparent electrophotographic layers for diapositives is of great interest[38]. The monomer of the binder (vinylcarbazole) is then polymerised in the presence of finely dispersed COA. This results in the formation of fairly homogeneous systems of the type of "solid solutions", which are suitable for the preparation of electrophotographic layers[37,38]. Copper organoacetylides have proved suitable for printing schemes involving the electrophotographic method, which ensure highly technological and economical set ups[40].

The first steps in the application of organometallic compounds in technology have shown that there are definite prospects and possibilities, the realisation of which depends to a considerable extent on how widely and deeply the electronic phenomena in this new class of semiconducting compounds will be investigated. Apart from the solution of technical problems, the study of the properties of organometallic solids may prove useful in relation to a wide range of problems associated with biocatalysis and carcinogenic activity[74].

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The data considered in this review show that organometallic compounds constitute a large and interesting class of new semiconducting compounds many of which effectively manifest a fundamental property such as the internal photoeffect. The possibility of a wide variation of the types of bonds by selecting the appropriate metals and ligands permits the reliable prediction that in the future the range of organometallic compounds with semiconducting properties will be greatly extended and that the study of the electronic phenomena in them will be vigorously continued.

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The Physics and Chemistry of the Reactions of Positrons and Positronium in Polymers

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The problems of the annihilation of positrons in polymers are discussed and the reactions of positrons and positronium, the effect of external electric and magnetic fields, and the influence of various kinds of radiation, temperature, pressure, phase transitions, etc. are examined. The practical value of the positron method for the investigation of polymers is demonstrated.
The bibliography includes 180 references.

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I. INTRODUCTION

During the last 10–15 years, there has been an appreciable growth of interest in the study of the reactions of positrons and positronium. The improvement of the experimental technique and methods and the increase of the resolving power of the apparatus, which have become possible as a result of advances in electronics, permitted fairly detailed observations of the reactions of positrons and positronium in matter. At the same time the observed high sensitivity of the characteristics of the electron–positron annihilation to the electronic structure, composition, and defects in the crystal structure of matter, temperature, pressure, phase transitions irradiation, and the effects of external electric and magnetic fields gave rise to the question of a new and in many instances unique method in the physics and chemistry of matter—the positron method.

The aim of the review is to give a systematic account and analyse the experimental and theoretical data, to discuss the main trends in research on the possibilities of the positron method in the physics and chemistry of polymers, and also to attract the attention of specialists in polymer science to the positron method. Without dwelling on the characteristics of the annihilation of positrons in various substances and on the description of the experimental technique and methods (see the relevant reviews, monographs, and corrections[1-15]), we shall proceed to the analysis of the reactions of positrons and positronium in polymers.

II. THE ANNIHILATION OF QUASI-FREE POSITRONS IN POLYMERS

1. The Characteristics of the Electron–Positron Annihilation

It has come to be believed that, as a result of various kinds of energy losses, the fast positrons which arise in the β^+-decomposition of the nuclei of radiative isotopes (^{22}Na, ^{64}Cu, and others) and pass into matter and are slowed down to thermal velocities (thermalisation) long before annihilation. During the retardation process, a proportion of the positrons form positronium. The fraction of positrons annihilated "in flight" is insignificant[2]. The average depth of penetration of positrons (^{64}Cu) is 370.4 ± 20.6 μm in polyethylene (PE) and 156.2 ± 6.1 μm in Teflon (PTFE)†.[15] If the spins of the particles are antiparallel (the singlet state of the e^+e^- pair), the 2γ-annihilation is most probable. On the other hand, for the parallel orientation of the spins of the particles (the triplet state of the e^+e^- pair), the minimum number of annihilation γ-quanta is three (3γ-annihilation). In the 2γ-annihilation the angle of dispersion of γ-quanta differs from π by an amount θ if the e^+e^- pair possesses momentum; the movement of the pair also leads to a Doppler shift ΔE_γ of the energy of the γ-quanta. The probability of the 2γ-annihilation of free particles per unit time in the non-relativistic approximation is, according to Dirac[17], $\lambda = \tau^{-1} = \pi r_0^2 cn$, where $r_0 = 2.818 \times 10^{-15}$ m is the classical radius of the electron, c the velocity of light, and n the number of electrons per unit volume.

The characteristics of the electron–positron annihilation (θ, ΔE_γ, and τ) correspond to the existing experimental methods based on the following measurements: (a) the angular distribution of γ-quanta in 2γ-annihilation (AD); (b) the distribution of γ-quanta in 2γ-annihilation in terms of the Doppler shift; (c) the time distribution of the annihilation radiation (TD); (d) TD corresponding to different angles θ (combined AD–TD method).

In the general case the TD spectrum consists of several components:

$$p(t) = \sum_i I_i \lambda_i e^{-\lambda_i t}, \quad (1)$$

where λ_i are decomposition constants ($\tau_i = \lambda_i^{-1}$ are the experimental average lifetimes of the positrons) and I_i are the

† Here and henceforth the following notation has been adopted: PE = polyethylene, PTFE = Teflon; PS = polystyrene; PVC = poly(vinyl chloride).

intensities of the components. The probability of the annihilation of the positron in a state i in a many-electron system per unit time with emission of two γ-quanta with an overall momentum p is given by the following expression in the one-particle approximation[18]: $\gamma_i(p) = \pi r_0^2 c \rho_i(p)$, where

$$\rho_i(\mathbf{p}) = \sum_j \left| \left(\frac{1}{2\pi\hbar}\right)^{3/2} \int \psi_i^+(\mathbf{r}) \psi_j \exp\left(-\frac{i}{\hbar}\mathbf{pr}\right) d\mathbf{r} \right|^2 \qquad (2)$$

is the function of the distribution density of the e^+e^- pairs being annihilated in terms of momenta, $\psi_i^+(\mathbf{r})$ is the wave function of the positron, and $\psi_j(\mathbf{r})$ are the one-electron wave functions of the atom (ion, molecule). The summation in Eqn.(2) is carried out over all the electrons in the system. The decomposition rate constant $\gamma_i = \sum_p \gamma_i(p)$ is given by

$$\gamma_i = \pi r_0^2 c n_i^*; \; n_i^* = \sum_j \int |\psi_i^+ \psi_j|^2 d\mathbf{r}, \qquad (3)$$

where n_i^* has the significance of the effective number of electrons for annihilation per unit volume of the substance. In the general case $\gamma_i \neq \lambda_i$.

The theoretical AD curves in the case of the isotropic distribution of the e^+e^- pairs in terms of momenta in the Steward approximation[19] can be calculated from the formula

$$I_i(\theta) = 2\pi \int_{p_z}^{\infty} \gamma_i(p) p \, dp; \; \theta = p_z/m_0 c,$$

where m_0 is the mass of the electron. The overall distribution is $I(\theta) = \sum_i I_i(\theta)$. The function of the distribution density of the pairs in terms of the momenta $\rho(p)$ and the momentum distribution of the pairs# $N(p)$ can be reproduced from the results of the measurement of the AD:

$$\rho(p) \propto -\theta^{-1} dI/d\theta, \quad N(p) = 4\pi p^2 \rho(p) \propto -\theta dI/d\theta.$$

We may also note that the decomposition constant γ_i is equal to the area under the theoretical $I_i(\theta)$ curve:

$$\gamma_i = m_0 c \int_{-\infty}^{+\infty} I_i(\theta) d\theta.$$

2. The Annihilation of Quasi-Free Positrons in Polymers

According to Gol'danskii[2], in the general case one can imagine three fundamental mechanisms of the annihilation of positrons in matter: (a) the annihilation of positrons in quasi-free collisions with the electrons of the surrounding medium; (b) the annihilation of positrons in different bound states of the non-positronium type arising on capture of thermalised positrons by ions, atoms, molecules, atom-molecule complexes, and defects; (c) the annihilation of positrons bound in positronium atoms.

In the annihilation of positrons in quasi-free collisions with (valence) electrons, one can infer the distribution densities of the valence electrons in space and with respect to momenta from the results of measurements of their TD and AD parameters. The rate of annihilation of slow quasi-free positrons in a molecular substance can be formulated as follows according to Eqn.(3):

$$\gamma_f = \frac{1}{\tau_f} = \pi r_0^2 c \frac{\rho}{M} N_A \sum_k \nu_k n_k^*, \qquad (4)$$

More precisely the distribution of the pairs with respect to momenta, but in the physics of slow positrons the term "momentum distribution of pairs" is used more often.

where ρ is the density, M the molecular weight, N_A the Avogrado number, ν_k the number of atoms (ions) of the kth kind in the molecule, and n_k^* the number of electrons in an atom (ion) of the kth kind which is effective for annihilation. For liquids and solids, $\gamma_f \cong 10^9$ s^{-1} according to Eqn.(4) and is proportional to the density of the substance. As an example, Table 1 presents the results of measurements[20,21] of the TD parameters (τ_i and I_i) for certain polymers.

Table 1. The average lifetimes of positrons (and the intensities of the TD components) relative to annihilation in certain polymers[20].

Substance	$10^{10}\tau_0$, s	$10^{10}\tau_1$, s	$10^{10}\tau_2$, s	I_0, %	I_1, %	I_2, %
Polystyrene	4.10±0.20	12.2±0.6	21.0±0.6	49±3	4.3±0.5	29.0±1.5
Polyethylene	3.20±0.12	7.7±0.3	27.4±0.8	61±4	15±1	22.8±1.2
Polyvinyltoluene	3.58±0.13	10.5±0.6	21.0±0.6	50±3	6.9±0.6	31.8±1.6
Polypropylene	3.46±0.10	9.9±0.5	23.5±0.7	74±4	7.5±0.7	14.6±0.8
Cellulose acetate	3.71±0.11	9.5±0.5	22.0±0.7	67±4	6.1±0.6	16.3±0.9
Lucite	3.20±0.10	8.2±0.4	19.6±0.6	63±4	11±1	22.0±1.1
Teflon (Ref.21)	3.3±0.1	9.7±0.5	40.9±0.3	64±4	15.0±1.9	21.0±0.4

Remarks: For polystyrene, polyvinyltoluene, and cellulose acetate, there is a component with $\tau_0' = 1.2 \times 10^{-10}$ and intensities of 18 ± 3, 14 ± 2, and 5.5 ± 0.7% respectively. In order to unify the notation, τ_0, τ_1, τ_2, and τ_3 have been replaced by τ_0', τ_0, τ_1, and τ_2 respectively.

Table 2. The number of electrons n_k^* effective for the annihilation of quasi-free positrons and the number of electrons z in the outer shell of the atom[20].

Atom	n_k^*	z	Atom	n_k^*	z
H	2.36±0.15	1	Si	11.2±0.3	4
B	4.5±0.2	3	S	11.7±0.4	6
C	5.08±0.22	4	Cl	11.4±0.3	7
N	6.6±1.4	5	Br	14.4±0.3	7
O	5.21±0.30	6	I	17.8±0.4	7

Cova and Zappa[20] suggested that $\tau_f = \tau_0 = 1/\lambda_0$ (or $\gamma_f = \gamma_0$) (we replaced the symbol τ_1 used by the above workers[20] for a short lifetime by τ_0). To test this hypothesis, we determined the number n_k^* for H, C, and O atoms from Eqn.(4) putting in the latter $\tau_f = \tau_0$ and substituting the experimental values of τ_0 for molecular liquids[22]. The values of n_k^* were then substituted in Eqn.(4) and the lifetimes τ_f in the polymers were calculated (these are listed in Table 1). It was found that $\tau_f = \tau_0$ to within 5%. The numbers of annihilation electrons calculated[20,22] from the lifetimes of positrons τ_0 in various substances are presented for a series of atoms in Table 2. Theoretically γ_f can be calculated in principle from Eqn.(3).

In the free positron approximation, we have

$$\psi^+(\mathbf{r}) = V^{-1/2} \exp(i\,\mathbf{kr}),$$

where V is the normalised volume and k the wave vector of the positron. For thermalised positrons, $\mathbf{k} \cong 0$ and the momentum distribution of the e^+e^- pairs

$$N(p) = \int_0^{2\pi} d\varphi \int_0^{\pi} \rho(p) p^2 \sin\vartheta \, d\vartheta$$

represents the momentum distribution of the electrons (in practice only valence electrons, in view of the inaccessibility of the inner regions of atoms to positrons).

The function $N(p)$ was calculated (by the method of Coulson and Duncanson[23-26]) by various workers[15,27-34] for low-molecular-weight substances (methane, benzene, hexane, etc.) in accordance with the scheme

$$N(p) = \sum_k \alpha_k N_k(p),$$

where α_k is the relative number of bonds of the kth type in the molecule, $N_k(p)$ is the momentum distribution of electrons in a bond of the kth type. The use of the Hartree–Fock wave functions for the 2s and 2p atomic orbitals of carbon instead of the Slater orbitals leads under these conditions to a much better agreement with experiment[28]. There is a discrepancy only in the region of momenta $p \cong (9-10) \times 10^{-3} m_0 c$. If account is taken of the distortion of the planar wave by the field generated by the atoms, in particular by the nuclei, it is possible to obtain a satisfactory agreement with experiment also in the region of large momenta[30-35]. [Fig.1; the appearance of a low-momentum component in $N(p)$ for liquid methane is associated with formation of positronium; see below]. The momentum distribution of the electrons of covalent bonds is insensitive to the fusion of the substance, as was to be expected (Fig.1).

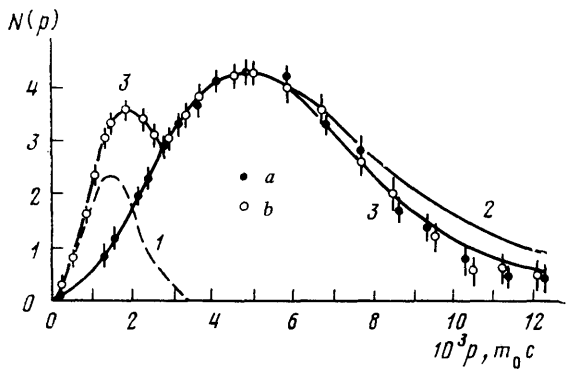


Figure 1. The momentum distribution $N(p)$ for e^+e^- pairs in methane according to AD measurements[30]: *a*) and *b*) experimental points for solid and liquid methane respectively; *1*) momentum distribution of parapositronium atoms; *2*) and *3*) $N(p)$ curves calculated in terms of the approximations of free positrons (curve *2*) and positrons interacting with atoms (curve *3*).

An analogous method can be applied in principle to the calculation of $N(p)$ and hence of the AD curve for high-molecular-weight substances. $N(p)$ for PE can be calculated comparatively simply if the bonds are assumed to be tetrahedral and the ratio of the number of electrons in the C–H and C–C bonds of the $[CH_2]_n$ molecule is assumed to be two in constructing the hybrid orbitals of the carbon atom. The results of the calculation of $N(p)$ and $I(\theta)$ for PE (with Hartree–Fock wave functions) are illustrated in Fig.2.

III. POSITRONIUM IN POLYMERS

1. The formation of Positronium

The properties of the positronium (Ps), i.e. a bound system consisting of an electron and a positron, *in vacuo* are well known (see sub-section 2). The Ps atom is a hydrogen-like atom with a reduced mass equal to $m_0/2$; its ionisation potential is $E_{Ps} \cong 6.77$ eV and its Bohr radius is $a_{Ps} = 2a_0 \cong 0.106$ nm (a_0 is the Bohr radius in the ground state of hydrogen). Parapositronium (*p*-Ps) undergoes spontaneous 2γ-annihilation at a rate $\lambda_s^0 = 8 \times 10^9$ s^{-1} (lifetime $\tau_s^0 = 1/\lambda_s^0 = 1.25 \times 10^{-10}$ s). Orthopositronium (*o*-Ps) is annihilated with emission of three γ-quanta at a rate $\lambda_t^0 = 7.14 \times 10^6$ s^{-1} (lifetime $\tau_t^0 = 1/\lambda_t^0 = 1.4 \times 10^{-7}$ s). As a consequence of the mixing of the substates $^1S_0$ and $^3S_1$ ($m = 0$), in a magnetic field the lifetime of orthopositronium is shortened (magnetic quenching of positronium). The "hydrogen-like" nature, the short lifetime, magnetic quenching, and the possibility of detecting even only one Ps atom [the real density of Ps atoms in matter in the course of the experiment is approximately 10^6 m^{-3} (!)] on the basis of the annihilation γ-quanta make positronium one of the unique research instruments in the physics and chemistry of matter.

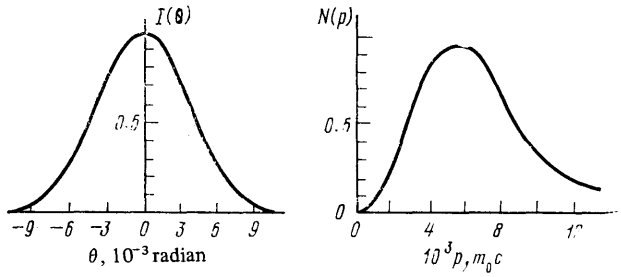


Figure 2. Theoretical AD curves $I(\theta)$ and the momentum distribution curves $N(p)$ for e^+e^- pairs in polyethylene.

The probability of the formation of positronium by retarded positrons in matter is "regulated" by energetic conditions. For a condensed phase, the so-called Ore gap or energy gap, within the limits of which the formation of positronium is most probable, is determined by the following inequality according to Ferrell[2,12,15]: $\mathcal{I} - E_{Ps} - Q_{Ps} < E_+ < E^* - Q_*$, i.e. the energetic condition for the formation and dynamic stability of positronium is represented by the inequality

$$Q_- + Q_+ < E_{Ps} + Q_{Ps},$$

where $\mathcal{I}$ is the ionisation potential and E^* the energy of the electronic excitation of the substance, E_+ the kinetic energy of the positron, and Q_-, Q_+, and Q_{Ps} are the affinities of the substance for the electron, the positron, and the Ps atom.

Even if there is no energetic prohibition of the formation of positronium, not all the positrons form positronium. Some of the positrons are annihilated within the limits of the Ore gap, are captured in non-positronium states ("adhere" to molecules, fall into traps, etc.), are retarded

to an energy $<E_+$ by non-elastic interactions, with individual molecules, etc. All these processes, which have been combined under the name of positronium inhibition processes, depend on the chemical composition, the intermolecular interaction, the structural defects, and other factors.

The so-called spur model of the formation of positronium, proposed[35] to account for the formation of positronium in liquids, has been widely discussed in recent years. It is assumed in this model that positronium is formed when a positron is bound to one of the electrons arising in the trace (spur) of the retarded positron as a result of the ionisation of molecules and accompanying ("escorting") the positron. For liquids (and solutions), it is possible to set up a quantitative theory of the reactions of positrons and positronium taking into account their interaction with the species in the trace of the positron (with electrons, ions, and radicals) and the surrounding medium (see, for example, Refs.15 and 35–41). Attempts have been made to apply the spur model to molecular crystals[36,42], but the problem of its applicability to molecular crystals and polymers has not been finally resolved[36].

2. The Quenching of Positronium

The interaction of positronium with the surrounding medium in matter leads to a significant alteration of its properties compared with a vacuum. Processes such as (a) pick-off annihilation, i.e. annihilation of the positron in the Ps atom by a "foreign" electron, (b) the ortho-para conversion ($^3S_1 \; ^1S_0$) in the interaction of Ps atoms with paramagnetic species M as a consequence (in the simplest case) of the direct spin exchange

$$M(\downarrow) + {}^3S_1(\uparrow\downarrow) \rightleftarrows M(\uparrow) + {}^1S_0(\uparrow\downarrow),$$

and (c) different kinds of chemical reactions of positronium with the molecules of the given substance (addition, substitution, and oxidation) alter the lifetime of positronium compared with τ_s^0 and τ_t^0. For orthopositronium, all the above processes, which open the channel to 2γ-annihilation, shorten the lifetime (compared with τ_t^0) and are therefore combined under the term "quenching" of positronium[2]. If we introduce the quenching rate constant λ_q, then usually $\lambda_t^0 \ll \lambda_q \ll \lambda_s^0$. Parapositronium is therefore relatively insensitive to the above processes. In the general case pick-off annihilation, which shortens the lifetimes of orthopositronium to $\lesssim 10^{-9}$ s, is most significant for polymers.

We shall consider the kinetics of the pick-off annihilation process. Suppose that the probability of the formation of positronium is P. Then at the initial instant $t = 0$ the probability of detecting the positron in a quasi-free state is $P_f(0) = 1-P$ and the probabilities of detecting positronium are $P_S(0) = \frac{1}{4}P$ in the singlet state and $P_t(0) = \frac{3}{4}P$ in the triplet state. The populations of the above states vary with time in accordance with the law

$$P_f(t) = (1-P)\,e^{-\lambda_f t}, \quad P_s(t) = \frac{1}{4}P\,e^{-\lambda_s t},$$
$$P_t(t) = \frac{3}{4}P\,e^{-\lambda_t t},$$

where $\lambda_s = \lambda_s^0 + \lambda_p$, $\lambda_t = \lambda_t^0 + \lambda_p$, λ_f is the rate of annihilation of quasi-free positrons, and λ_p is the rate of pick-off annihilation. The TD spectrum consists of three components with the average durations $\tau_0 = \lambda_s^{-1}$, $\tau_1 = \lambda_f^{-1}$, and $\tau_2 = \lambda_t^{-1}$ and with the intensities $I_0 = \frac{1}{4}P$, $I_1 = 1-P$, and $I_2 = \frac{3}{4}P$. If the TD components with the decomposition constants λ_s and λ_f cannot be resolved, the experimental (average) short lifetime is

$$\tau_1 = \frac{1}{I_1}\left(\frac{I_f}{\lambda_f} + \frac{I_s}{\lambda_s}\right),$$

and $I_1 = I_f + I_S$.

Since the momentum of the p-Ps atom retarded to thermal velocity is comparatively small, the self-annihilation of parapositronium contributes to the AD curve in the region of small angles, while a comparatively narrow peak appears on the AD curve—a narrow $N(\theta)$ component and a low-momentum component on the $N(p)$ curve (see Figs.3 and 4 and also Fig.1). The intensity $I_N = \lambda_S^0 \int_0^\infty P_S(t)dt$ of the narrow AD component is

$$I_N = \frac{1}{4}P\,\frac{\lambda_s^0}{\lambda_s^0 + \lambda_p} \approx \frac{1}{3}I_2, \qquad (5)$$

since usually $\lambda_p \ll \lambda_S^0$. The annihilation of free positrons and the pick-off annihilation of positronium give rise to the broad AD component.

The relative probabilities of the 3γ-annihilation of quasi-free positrons and orthopositronium are $P_{3\gamma}^0 = 1/372$ (Gol'danskii[2]) and $P_{3\gamma}^t = \lambda_t^0 \int_0^\infty P_t(t)dt$ respectively and the overall probability of 3γ-annihilation is therefore

$$P_{3\gamma} = I_2\frac{\tau_2}{\tau_t^0} + \frac{1}{372}\left(1 - \frac{4}{3}I_2\right).$$

The inequality $P_{3\gamma} > P_{3\gamma}^0$ is an "indicator" of the formation of positronium in matter. In polymers $P_{3\gamma} > P_{3\gamma}^0$ (see, for example, Refs.7 and 45–47). Thus we have $P_{3\gamma}/P_{3\gamma}^0 \cong 2.60$ for PTFE and $P_{3\gamma}/P_{3\gamma}^0 = 3-4$ for rubbers[7].

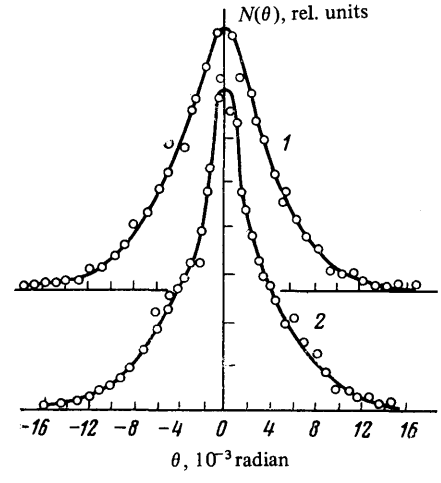


Figure 3. AD curves for Teflon recorded at 77 K (curve *1*) and 525 K (curve *2*).[43]

The positronium formed in the given substance is thus manifested experimentally by the appearance of a long-lived component in the TD and a narrow component in the AD and also by the higher probability of 3γ-annihilation $P_{3\gamma}$ compared with $P_{3\gamma}^0 \cong 0.27\%$. At the same time the relevant measurements make it possible to follow the reactions

of positronium in the substance and its properties on the basis of the TD and AD parameters and $P_{3\gamma}$.

If parapositronium is thermalised and exists in a free state, then its momentum distribution is Maxwellian:

$$N(p) \sim p^2 \exp(-p^2/4m_0k_0T),$$

while the narrow component of AD has a Gaussian form:

$$N(\theta) \sim \exp(-m_0c^2\theta^2/4k_0T).$$

The width of the $N(\theta)$ distribution profile at half its height at the maximum (the half-width of the narrow component) is $\Gamma_N \cong 4.33 \times 10^{-2} T^{1/2}$ mrad. At 295 K we have $\Gamma_N \cong 0.74$ mrad, so that the distribution $N(\theta)$ should be indeed manifested in the given instance by a very narrow peak in the AD. However, in polymers such a narrow distribution is usually not observed.

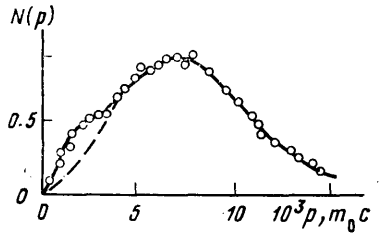


Figure 4. The momentum distribution of e^+e^- pairs in Teflon at room temperature[44] [dashed curve—theoretical calculation of the $N(p)$ function in the region of low values of p].

3. The States of Positronium in Molecular Substances. The "Positronium Capture Model"

There is reason to believe[10,48-51] that positronium can exist in a condensed phase in two states: the quasi-free or delocalised state and the localised state. The localised state arises in the "capture" of a Ps atom by a trap, whose role may be assumed by a macrocavity, a region of reduced density, etc. Bearing in mind that $\lambda_t^0 \ll \lambda_s^0$ and assuming that $\lambda_f \cong \lambda_p$, $\lambda_{pv} \ll \lambda_s^0$, $\lambda_t^0 \ll \lambda_{pv}$, and $\lambda_t^0 \ll \lambda_p + k$, where λ_p and λ_{pv} are respectively the rates of the pick-off annihilation of the quasi-free and localised positronium and k is the rate constant for the capture of positronium by traps, Bartenev and coworkers[49,50] interpreted the observed TD components (when the spectrum was resolved, as usual, into three components) as follows. The long-lived component τ_2 corresponds to the annihilation of o-Ps atoms in a trap, the intermediate component τ_1 corresponds to the annihilation of free positrons, and the short-lived component τ_0 corresponds to the annihilation of o-Ps atoms in a free state and of the p-Ps atoms in free and localised states. The parameters of the experimental TD spectrum are related to the parameters of the model as follows[49,50]:

$$\tau_0 = \frac{1}{4 - 3k/\Lambda_p}\left[\frac{k}{\Lambda_p}\left(\frac{1}{\lambda_{so}} - \frac{1}{\lambda_s} - \frac{3}{\lambda_t}\right) + \frac{1}{\lambda_s} + \frac{3}{\lambda_t}\right],$$

$$\tau_1 = 1/\lambda_f, \quad \tau_2 = 1/(\lambda_t^0 + \lambda_{po}) \approx 1/\lambda_{po},$$

$$I_0 = 1 - I_1 - I_2, \quad I_1 = 1 - P, \quad I_2 = 3/4Pk/\Lambda_p,$$

where $\Lambda_p = \lambda_p + k - \lambda_{pv}$, $\lambda_{sv} = \lambda_s^0 + \lambda_{pv} \cong \lambda_s^0$, $\lambda_s = \lambda_s^0 + \lambda_p + k$, and $\lambda_t = \lambda_t^0 + \lambda_p + k \cong \lambda_p + k$. The form of the narrow AD component is defined by the expression

$$N(\theta) = (\lambda_{so}/\lambda_s) N_f(\theta) + (k/\lambda_s) N_v(\theta),$$

where the $N_f(\theta)$ and $N_v(\theta)$ components are due to the self-annihilation of the quasi-free and localised parapositronium. The intensity of the narrow component is $I_N \cong \frac{1}{4}P[1-(k/\lambda_s^0)]$.

If the τ_1 component is attributed to the annihilation of free positrons, as suggested by Bartenev and coworkers[49,50], then it is difficult to explain the reason for the long lifetime (for example 1.22 ns in PS; see Table 1) of this fraction of positrons. Furthermore, it follows from the calculations of Cova and Zappa[20] (see above) that $\lambda_f^{-1} \cong \tau_0$. Judging from the value of τ_1, the τ_1 component can be due to the faster, than in the case of the τ_2 component, pick-off annihilation of orthopositronium. There is then a possibility of several versions. For example, traps in the crystalline and amorphous regions of the polymer have different constants λ_{pv} and k (we shall denote them respectively by λ'_{pv}, k, and λ_{pv}, k) and $\lambda_{pv} < \lambda'_{pv}$. Positronium is formed and annihilated, remaining in its own region—crystalline or amorphous. Then $\tau_1 \cong (\lambda'_{pv})^{-1}$, $\tau_2 \cong \lambda_p^{-1}$, $I_1 = 3\chi Pk'/4\Lambda'_p$, and $I_2 = 3(1-\chi) \cdot Pk/4\Lambda_p$, where $\Lambda'_p = \lambda'_p + k' - \lambda'_{pv}$ and $\Lambda_p = \lambda_p + k - \lambda_{pv}$, while χ is the degree of crystallinity of the polymer. In the more general case account may be taken of the "escape" of the Ps atoms from the traps and their diffusion from one region of the polymer to another[52-56]. We shall return to the problem of the nature of the τ_1 component in discussing experimental data.

IV. THE INFLUENCE OF TEMPERATURE, PHASE TRANSITIONS, AND PRESSURE ON THE PROPERTIES OF POSITRONIUM IN POLYMERS. THE "FREE VOLUME" MODEL

1. The Effect of Density in the Quenching of Positronium in Polymers. The "Free Volume" Model

The shortening of the lifetime of the long-lived component (τ_2) of TD with decrease of temperature[57] (for example, $\tau_2 = 3.5$, 2.5, and 1.6 ns for PTFE at 20°, −78°, and −196 °C), the enhancement of the narrow AD component on heating polymers[43,58] (see, for example, Fig. 3), and finally a decrease of the intensity of the narrow component (for PTFE[58]) and at the same time of τ_2(lucite, PTFE, and PE at pressures up to 1.01 GPa)[59] were originally observed in earlier investigations. The decrease of τ_2 both with decrease of temperature and following the compression of the test substance is interpreted as a density effect, i.e. as a consequence of the increase of the density and hence of the decrease of the "free volume" (i.e. of the interstitial volume, the volume of microcavities, the volume of regions with a reduced density, etc.) in which the Ps atom is "located".

The dependence of τ_2 on the "free volume" can be accounted for on the basis of a simple model of the interaction of a Ps atom in a trap with the surrounding medium—as a species with a mass $2m_0$ in the potential well[58,60]. The probability $\mathscr{P}$ of the Ps atom being outside the well, i.e. in the given substance, is determined by the shape, size, and depth of the well. The overlap of the wave function $\psi(\mathbf{R})$, describing the movement of the centre of inertia of the Ps atom, with the wave functions of the surrounding molecules, and therefore the rate of pick-off annihilation of positronium increase with decrease of the size of the well, i.e. of the "free volume", and τ_2 correspondingly decreases. The rate of pick-off annihilation in the "free volume" model can be

formulated thus:

$$\gamma_p = \mathcal{P}\gamma_0;\ \mathcal{P} = 1 - \int_{v_f} |\psi(\mathbf{R})|^2 d\mathbf{R}, \qquad (7)$$

where $\gamma_0 = \pi r^2 c n^*$, v_f is the "free volume" (the volume of the trap), and n^* is the electron density in the given substance effective for the pick-off annihilation of positronium. $n^* = 3.8 \times 10^{29}$ m^{-3}, which corresponds to the electron density in the region where the positron is present in the P$\bar{s}$ ion ($\tau^0 = \gamma_0^{-1} = 0.35$ ns), is frequently chosen for estimates. Calculations of $\mathcal{P}$ have been carried out[61-71] for various geometries of the free volume: spherical (Figs.5*a* and 5*b*), cylindrical (Figs.5c), and planar (Fig.5d).

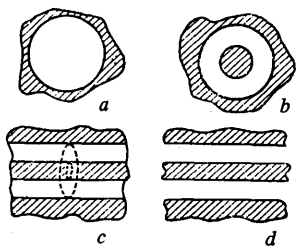


Figure 5. Different geometries of the free volume: *a*) and *b*) spherical geometry; *c*) cylindrical geometry; *d*) planar geometry.

2. Brandt's Free Volume Model

According to Brandt et al.[61,63,64],

$$\mathcal{P} = \frac{1 + G\{\exp[2\xi^2(S, v^*)\langle u^2(T)\rangle/R_0^2] - 1\}}{1 + F(S, v^*)}, \qquad (8)$$

where $S = (4m_0/\hbar^2)U_0R_0^2$ is a dimensionless parameter proportional to the height of a rectangular potential U_0 and the square of the radius R_0 of the core of the cell (i.e. the "excluded" volume v_0) and $v^* = v_1/v_0$ is the reduced "free volume", while v is the volume of the entire cell with a radius R_1 (in the range $R_0 \leq R \leq R_1$ we have $U_0 = 0$ and $n^* = 0$ and the cell constitutes the intrinsic "free volume" $v_f = v_1 - v_0$); the factor G varies from 1/2 to 1 and is approximately given by

$$G \simeq 1 - \frac{1}{2}\, t\hbar\, \frac{\mu - 1}{\xi(S, v^*)},$$

where u = 1, 2, or 3 for the planar, cylindrical (chain), and spherical geometries of the cell respectively. The temperature variation of the reduced mean-square amplitude $\langle\mu^2\rangle/R_0^2$ of the vibrations of the core in the region $\Theta_D \leq T \leq T_m$ is given by the expression

$$\langle u^2\rangle/R_0^2 = v^{*2/\mu}\gamma_m T/T_m,$$

where γ_m is the critical value of $\langle u^2\rangle/R_0^2 v^{*2/\mu}$ attainable on fusion and Θ_D and T_m are respectively the Debye temperature and the melting point. For a melt (T/T_m),

$$\langle u^2\rangle/R_0^2 \simeq v^{*2/\mu}\gamma_m.$$

If $T < \Theta_D$, then $\langle u^2\rangle \cong$ const. and $\mathcal{P}$ depends only on the model parameters S and v^*: $\mathcal{P}[1 + F(S, v^*)]^{-1}$.[71] The functions $\xi(S, v^*)$ and $F(S, v^*)$ have been expressed[64] in analytical and graphical forms. Interpolation formulae for ξ and F are[64]

$$\xi^2(S, v^*) = S[1 - (1+F)^{-2/3}],$$

$$F(S, v^*) = \frac{4}{\pi^3}\{[1 + S^{1/2}(v^{*1/\mu} - 1)]^3 - 1\}.$$

The half-width of the narrow AD component in the free volume model can differ appreciably (is greater) from Γ_N for free thermalised positronium. (The experimentally observed broadening of the narrow component relative to Γ_N for thermalised positronium has served as a basis for the authors' hypothesis[58] concerning the possible localisation of Ps atoms). In Brandt's "free volume" model the half-width of the component (in mrad) is[71]

$$\Gamma_N \simeq 0{,}25 g_\mu^{1/3} \frac{S^{1/2}}{R_0}\left(\frac{\gamma_p}{\gamma_0}\right)^{1/3}, \qquad (9)$$

where $g_\mu = \frac{1}{2}\mu$ for $\mu = 1$ and 2 and $g_\mu = 1/\mu$ for $\mu = 3$; R_0 is measured in nanometers. Thus a relation has been established between Γ_N and γ_p.

3. The "Empty Free Volume" Model (The "Trap" Model).

In the region where the Ps atom is localised is regarded as spherical without a "core" (Fig.5*a*) and the interaction of the Ps atom with the surrounding medium is modelled by a rectangular spherically symmetrical potential well with a radius a and a depth U_0, then $\mathcal{P} = k^2/\alpha(\alpha + aP_0 + k^2/\alpha)$, where $k = (2/\hbar)(m_0E)^{1/2}$, $\alpha = (2/\hbar)[m_0(U_0 - E)]^{1/2}$, $P_0 = (4/\hbar)m_0U_0$, and E is the energy of the Ps atom in the well[65]. Bearing in mind that $\mathcal{P} = \gamma_p/\gamma_0$ and assuming that $E \cong \frac{1}{16}m_0c^2\Gamma_N$, in this model the parameters of the well (or the trap of the Ps atom if the terminology of the "positronium capture" model is used) can be estimated from the experimental values of γ_p and Γ_N as $a \cong 0.77\chi/\Gamma_N$ nm and $U_0 \cong 3.2 \times 10^{-2}(\Gamma_N/y)^2$ eV, where Γ_N is expressed in milliradians and x and y constitute the solution of the equations

$$y = \sin x, \quad \gamma_p/\gamma_0 = y^3/[y + x(1 - y^2)^{1/2}]$$

for $\cot x < 0$. In a more rigorous solution of the problem, one calculates in the first place the narrow AD component and then its half-width is determined. For an infinitely deep spherically symmetrical rectangular potential well, the wave function of the Ps atom is

$$\psi(\mathbf{R}) \sim \sin kR/R,$$

and the angular distribution of the annihilation γ-quanta assumes the form

$$N(\theta) \sim \int_\beta^\infty \left(\frac{\sin z}{\pi^2 - z^2}\right)^2 \frac{dz}{z};\ \beta = \frac{m_0 c a}{\hbar}\theta.$$

Numerical calculation of the width of the $N(\theta)$ distribution profile at the level of half its height at the maximum yields[72] $\Gamma_N \cong 1.660\, a^{-1}$ mrad, where a is expressed in nanometers. The $N(\theta)$ distribution for a spherical well with a finite depth[72] and also for a rectangular potential box[73] has also been discussed. The parameters of the well can be determined also from the form of the $N(p)$ momentum distribution[15,67].

4. Dependence of the "Positronium Parameters" of AD and TD on Temperature and Pressure in Polymers and the "Free Volume" Model

Studies on the temperature and pressure dependence of the AD and TD parameters, associated with the reactions of positronium, in various polymers have on the whole confirmed

the conclusions derived from the "free volume" model[1,2,57-63,66,74-87].

In a study[62] of the dependence of the parameters τ_2 and I_2 of the long-lived TD component (the TD component decomposed into two components) on temperature (up to 200 °C) and pressure (up to 6.06 GPa), a relation of the following type was established for a number of substances:

$$\tau_2 \simeq \tau_2^0(T)(1-\eta\Delta V/V_0).$$

Here $\Delta V = V_0 - V$ is the volume change under the influence of pressure. The values of τ_2^0 (30 °C) and η, determined from the experimental data, are as follows:

Polymer	Lucite	PTFE	PS
τ_2^0 (30° C), ns	1.7 ± 0.2	3.2 ± 0.2	2.2 ± 0.2
η	4.3 ± 0.9	5.0 ± 0.8	4.3 ± 0.7

Having formulated $\tau_2^{-1} \cong \mathcal{P}\gamma_0$ [see Eqn.(7)] and having defined as the probability that the Ps atom is located outside the limits of a three-dimensional rectangular potential well with a volume v ($\mathcal{P} \propto v^{-0.87}$), so that $\tau_2 \propto v^{0.87}$, the authors[62] based their treatment in essence to the "empty free volume" model. Hence, if one assumes on the basis of compressibility data for polymers that the fraction of vacancies in non-compressed polymers is 20%, it follows that[62]

$$\tau_2 = \tau_2^0(1-5\Delta V/V_0)^{0.87},$$

which corresponds to $\eta = 4.35$ in the empirical $\tau_2(V)$ relation. The calculated and experimental values of η agree within the limits of the error of the measurements.

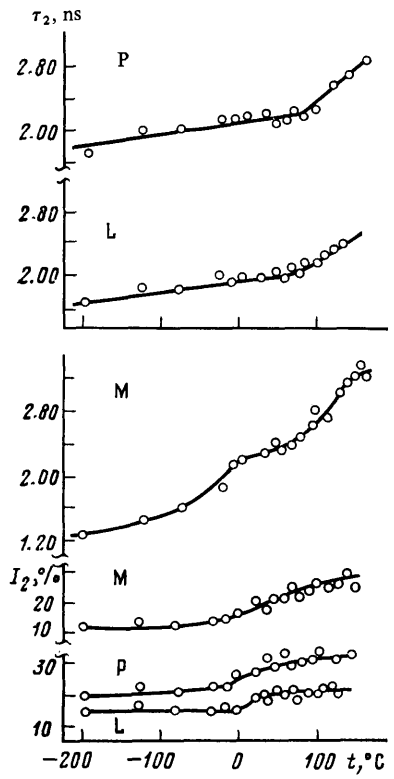


Figure 6. Dependence of the parameters of the long-lived TD component (the lifetime τ_2 and the intensity I_2) in polystyrene (P), lucite (L), and Marlex-50 polyethylene (M).[76]

The ratio I_2/I_2^0 for polymers decreases as the substance is compressed, which, however, is not obligatorily related to the decrease of the probability of the formation of positronium and may be caused, according to the "positronium capture model" [see Eqn.(6)] by the corresponding change in the parameters k, λ_p, and λ_{pv} ($k \propto n$, where n is the number of traps per unit volume of the polymer and λ_p and λ_{pv} are determined respectively by the density of the polymer and the volume of the traps). The decrease of τ_2 in polymers with decrease of temperature and the breaks in the $\tau_2(T)$, $I_N(T)$, and I_2 curves in the region of phase and relaxation transitions[1,2,15,66,76,79,82-86] (Figs. 6 and 7) are also qualitatively consistent with the "free volume" model. The glass points determined from the positronium data are somewhat lower than those found by other methods, which indicates a higher sensitivity of the positronium method to changes in the structure of the polymer[84,86]. In the region of vitrification I_2 is almost independent of temperature[1,75,84,86], i.e. the increase of the size of the microcavities is not accompanied by an appreciable change in their number.

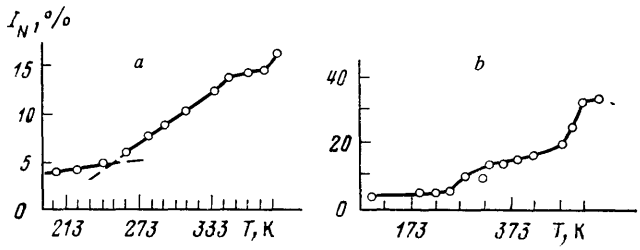


Figure 7. Temperature dependence of the intensity of the narrow AD component in high-pressure polyethylene (*a*) and in Teflon with a degree of crystallinity of 64% (*b*).

One of the causes of the appearance of breaks in the $\tau_2(T)$ curves is "vibrational" movement of atoms (and molecules) and the fluctuations in the density of the substance caused thereby, which lead to the "smearing" of the electron density and hence to an increase of the rate of pick-off annihilation of orthopositronium in contrast to the "free volume" effect, due in this instance to thermal expansion. These effects have been analysed quantitatively[63,70] (they are "inherent" in Brandt's "free volume" model—see above). In polymers the smearing of electron density and hence the associated acceleration of the pick-off annihilation of positronium can arise when the mobilities of particular kinetic units are "switched on" in the temperature range of the relaxation transitions on heating the polymer[51,85].

The TD spectra in polymers contain up to three (or even up to four) components[24,63,87-89] (Table 1). Having measured the temperature dependence of the TD parameters in PE and PTFE (and also in glycerol), Brandt and Spirn[63] concluded that the component τ_2 is due to the pick-off annihilation of the *o*-Ps atoms in the disordered regions of the polymer, while the component τ_1 is due to the annihilation of free positrons; the *p*-Ps atoms located in the disordered regions and the *o*-Ps and *p*-Ps atoms in the ordered regions contribute to the component τ_0. We may note that an analogous interpretation of the TD spectrum has been adopted by the authors of the "positronium capture" model (see Section III).

Fig. 8 presents the experimental values of τ_2 for PE and PTFE and the calculated $\tau_2(\nu^*) = 1/\gamma_p(\nu^*)$ curves based on Eqns. (7) and (8) for $\mu = 2$, $S = 25$, and $\gamma_m = 1/16$ and 1/12 respectively. Extrapolation of the data in Fig. 8 to close packing conditions yields values of τ_2 close to τ_0, which, as it were, confirms the validity of the hypothesis concerning the relation between τ_0 and the pick-off annihilation of positronium in the ordered domains of the polymer. In a subsequent study[71] dealing with the TD spectrum in paraffins, including PE, the above interpretation was wholly retained. At the same time it is assumed that the component τ_1 of TD involves the contribution of the positrons located in the disordered domains in the form of A_+ centres[90] (see also Refs. 6, 9, 10, and 12); on the other hand, the annihilation of free positrons contributes to the component τ_0. According to Brandt[71], the half-width of the narrow AD component in paraffins [see Eqn. (9)] is $\Gamma_N \approx 3.5$ mrad. Measurement of Γ_N for PE yields the same value[82].

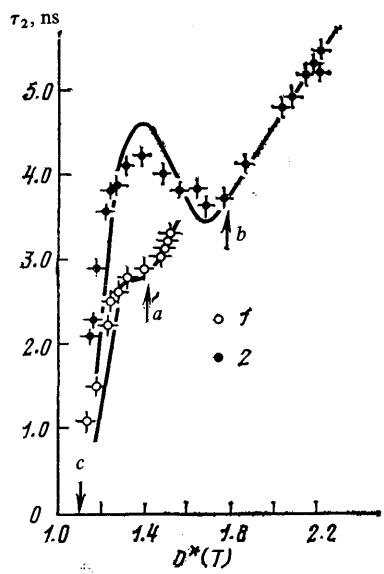


Figure 8. Dependence of the lifetime of positronium τ_2 on the reduced free volume $\nu^*(T)$ in polyethylene (*1*) and Teflon (*2*);[63] symbols—experimental data; curves—calculation; *a*) and *b*) $\nu^*(T_m)$, where T_m = melting point; *c*) close packing.

Thus the dependence of the TD (and also AD) parameters on the reduced "free volume" in molecular substances, including polymers, has been given the same treatment in studies by Brandt and coworkers[63,71]. Nevertheless one must bear in mind that there are discrepancies in the experimental data of different workers (cf. for example, the data in Refs. 63 and 75, on the one hand, and Ref. 77 on the other). The definition of τ_0 as the average lifetime of free positrons or positrons bound in A_+ centres, adopted by Brandt and coworkers[63,71] (see above), is also open to objection. Whereas according to Brandt and coworkers[63,71] the value of τ_0 in PE and PTFE is independent of temperature and that in PE is independent of the degree of crystallinity (Table 3), according to, for example, the data of other workers for PTFE [89] and PE [1,15,91] this is not the case.

Finally, one must bear in mind the approximate nature of the "free volume" model itself, associated with the choice of the form of the potential of the interaction of the Ps atom with the surrounding medium, with the uncertainty of the electron density n^* effective for pick-off annihilation [see Eqn. (7)], with neglect of the details of the formation and reactions of positronium preceding its localisation (such as the probability of the formation of positronium in the crystalline and amorphous region of the polymer, the nature of the population of the "free volumes" by Ps atoms—gas-kinetic or diffusional, etc.), and other factors.

Table 3. Dependence of the TD parameters for polyethylene on the degree of crystallinity χ of the specimens[71] (ρ = density; ν^* = reduced "free volume").

χ, %	$10^{-3}\rho$, kg m^{-3}	ν^*	τ_0, ns	I_0, %	τ_1, ns	I_1, %	τ_2, ns	I_2, %
46	0.917	1.298	0.31	63	0.65	10	2.61	27
51	0.925	1.290	0.33	67	0.81	9	2.67	24
53	0.930	1.280	0.31	69	0.87	9	2.54	22
69	0.948	1.255	0.32	72	0.80	10	2.53	18
80	0.967	1.231	0.34	73	0.75	9	2.54	18

V. DEPENDENCE OF THE PROPERTIES OF POSITRONIUM ON THE STRUCTURE AND DEGREE OF CRYSTALLINITY OF POLYMERS

In the "free volume" model it is in essence assumed that the overall probability of the formation of positronium in molecular substances is independent of temperature, state, and structure. However, numerous experiments (see, for example, Refs. 2, 6, 8, 42, and 92–96), involving observation of the formation of positronium in molecular substances (and in ionic compounds) indicate the opposite behaviour in crystal–liquid and crystal–glass transitions when the conditions and nature of the preliminary treatment are altered. The same applies also to polymers[1,2,15,77,78,80,82–84,91,97–101].

In PTFE with a lower degree of crystallinity (~44%) and density (2.14×10^3 kg m^{-3}), obtained by the rapid cooling of specimens heated to 350 °C, the intensity of the long-lived component $I_2 \approx 23.8\%$ and the sum $I_1 + I_2 \approx 33.1\%$ proved to be appreciably higher than in PTFE with a higher degree of crystallinity (~76%) and density (2.26×10^3 kg m^{-3}), obtained by slow cooling: $I_2 \approx 6.9\%$ and $I_1 + I_2 \approx 21.9\%$.[89] The conversion of PTFE into an amorphous form entails an increase by 6.3% of the fraction of the narrow component in AD.[97]

Later measurements of TD and AD in polymers (PE, PTFE, PS, nylon, and lucite) confirmed the sensitivity of the TD and AD components, bound to positronium, to the degree of crystallinity (Table 3) and to the configuration and conformation of the molecular chains of polymers[1]. In particular, it has been observed[100] that, on passing to a PE "single crystal", the narrow component in AD virtually disappears. Studies on polymeric systems based on epoxy-resins[15,84,86] demonstrated a high sensitivity of the TD parameters to the microstructure of the free volume. According to Grinev et al.[84], the positron method is at present apparently most promising for the study of the microstructure of the free volume of polymers.

In order to elucidate the nature of the long-lived components in molecular substances, attempts have been made[102–105] to employ the combined AD–TD method. Thus McGervey and

Valters[105], who studied PTFE by this method, concluded that the component τ_1 is due to the annihilation of free positrons (the hypothesis of Brandt and Spirn[63]) or the positrons linked to the PTFE molecules. According to Kerr's measurements[44], $I_N \cong I_2/3$ for PTFE and PE. Hence the author concludes [see Eqn.(5)] that only the τ_2 component of TD is due to orthopositronium. On the other hand, other investigators[89,97,99] attribute the component τ_2 to the pick-off annihilation of the *o*-Ps atoms in the amorphous regions and τ_1 to the pick-off annihilation in the crystalline domains of the polymer, i.e. they believe that the ratio $I_1/(I_1+I_2)$ can serve as a measure of the crystallinity of the polymer. The same view is maintained by other investigators[15,86,91]. However, one cannot rule out the possibility that both views on the nature of τ_1 are to some extent valid if it is assumed that a positron–many-electron system, capable of being positronium-like to some extent, can be formed in the polymer. In the simplest case such a system can consist of a positron–exciton complex (see also Section III, sub-section 1).

Chandra and coworkers[106–109] drew attention to a correlation between I_2 and τ_2: a lower intensity corresponds to a longer lifetime and the points on the $I_2-\tau_2$ diagram are arranged in groups, one of which corresponds to liquids, another to polymers, and a third to crystals (Fig.9). According to the "free volume" and "positronium capture" models, the above correlation is due to the fact that γ_p (and hence also τ_2) are determined by the elementary free volume v_f and $I_2 \propto V_f/v_f$, where V_f is the overall free volume. As a result, it is possible to obtain a relation of the type[107,108]

$$I_2 = a'(1+\ln(\tau_2/\tau_c))/[b+\ln(\tau_2/\tau_c)],$$

where a', b, and τ_c are the parameters of the model and $a' \propto v_f$. The theoretical curves in Fig.9 were calculated for $\tau_c = 0.7$ ns, $b = 0.01$, and $a' = 3.375$ (crystals), 12 (polymers), 17 (liquids), and 25 (amorphous bodies).

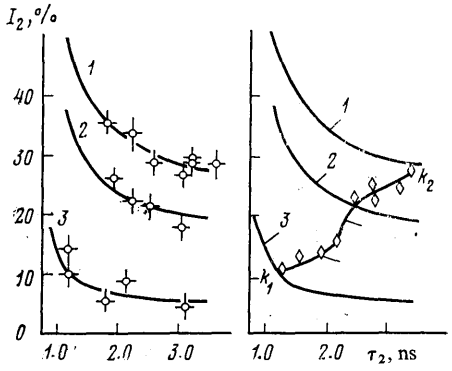


Figure 9. $I_2-\tau_2$ diagrams for simple unassociated liquids and amorphous substances including polystyrene and fused quartz (*1*), partially crystalline substances—poly(vinyl chloride), polyethylene, lucite, and Teflon (*2*), and molecular crystals (*3*); circles—experimental data; lines–calculated data; (*4*) the values of I_2 and τ_2 for Marlex-50 in the range from −196 °C (point k_1) to 142 °C (point k_2).

We shall now quote certain results obtained[49,50] with the aid of the "positronium capture" model. The solution of Eqn.(6) with experimental TD parameters for PTFE with different degrees of crystallinity χ [89] yields $k_1 = (0,32 \pm 0.05) \times 10^9$ s^{-1} and $\lambda_{p1} = (2.5 \pm 0.4) \times 10^9$ s^{-1} for $\chi_1 = 76\%$ and $k_2 = (0.67 \pm 0.10) \times 10^9$ s^{-1} and $\lambda_{p2} = (1.7 \pm 0.3) \times 10^9$ s^{-1} for $\chi_2 = 44\%$. The expected difference $\Delta I_N = I_N(\chi_2) - I_N(\chi_1) = 6 \pm 1\%$ between the intensities of the narrow components, calculated using these constants, agrees with the measured value[97]: $\Delta I_N = 6.3 \pm 0.4\%$. If we put $k = \sigma\bar{v}n$, where σ is the capture cross-section and $\bar{v}$ the average velocity of the thermal movement of the Ps atoms, then, under conditions such that $n \cong (1-\chi)n_a$, where n_a is the bulk density of traps in the amorphous region of the polymer, we have (provided that n_a is independent of χ) $k_1/k_2 = (1-\chi_1)/(1-\chi_2)$, which is confirmed by the above data: $k_1/k_2 \cong 0.48$ and $(1-\chi_1)/(1-\chi_2) \cong 0.43$. If the equilibrium concentration of traps n in the polymer obeys the Arrhenius law, i.e. $n \propto \exp(-E_a/k_0T)$, where E_a is the activation energy for the formation of traps, then the temperature variation of the rate of capture is largely determined by the factor n (Fig.10). The change in the slopes of the $\ln k - 1/T$ linear plots in phase transitions is apparently associated with the change in the activation energy E_a.

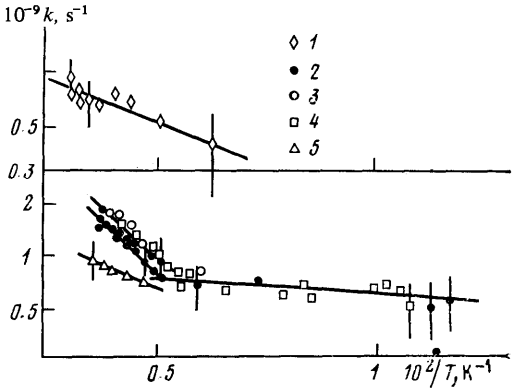


Figure 10. Dependence of the rate constant k for the capture of positronium on the reciprocal of temperature (on the semilogarithmic scale) in Teflon (*1*), polyethylene (*2–4*), and glycerol (*5*) plotted[49] on the basis of data from a series of investigations[49,63,76].

Using the results of TD and AD measurements and the "empty free volume" model (see Section IV, subsection 3) and the "positronium capture model" (see Section IV, subsection 4), Bartenev et al.[50] estimated the radius of the traps, the capture rate constant k, and the bulk density of traps n in high-pressure PE of two types—PEA (autoclave reactor) and PET (tubular reactor). The relation $\sigma = \pi a^2$ was used to estimate n from the measured values of k: $a = 0.45 \pm 0.05$ nm, $k = 1 \times 10^9$ s^{-1} (±30%), and $n = 0.15 \times 10^{22}$ m^{-3} for PEA, and $a = 0.34 \pm 0.05$ nm, $k = 4 \times 10^9$ s^{-1} (±30%), and $n = 1.1 \times 10^{22}$ m^{-3} for PET.

The temperature effects of the annihilation of positrons in polymers do not reduce solely to those discussed above. The TD (I_2 and τ_2)[1,84,110,111] and AD (I_N) [51] parameters are influenced significantly by the thermal degradation of the polymer, since the free radicals arising in this process cause additional quenching of orthopositronium (see below). In the solution

of the problems considered here (and in the previous Section), general approaches have so far been outlined; there is still a need for much tedious theoretical and experimental work in order to achieve an unambiguous quantitative utilisation of the results of measurements of TD and AD parameters in the physics and chemistry of polymers. The results of studies of the reactions of positronium in molecular[42,112–115] and liquid crystals[116–120], haemoglobin[121], aminoacids[122], optical isomers[122,123], etc. may prove to be not without interest from this point of view. In molecular crystals the reactions of positronium are influenced significantly by phase transitions, structural defects, impurities, and the form of the free volume. In liquid crystals the TD parameters (I_2 and τ_2) undergo considerable sudden changes at the phase transition points, and in the isotropic liquid → liquid crystal phase → crystal transitions τ_2 increases abruptly for liquid crystals with negative dielectric anisotropy ($\varepsilon_a < 0$) and conversely decreases for liquid crystals with $\varepsilon_a > 0$. In aminoacids a difference has been observed between the values of I_2 and τ_2 for D- and L- isomers, the sign of the differences ΔI_2 and $\Delta\tau_2$ being positive for some aminoacids and negative for others.

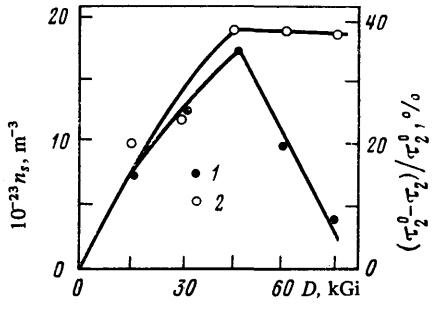


Figure 11. The relative decrease of τ_2(*1*) and the change in the concentration of free radicals (*2*) in Teflon with increase of the dose of irradiation with ^{60}Co γ-rays (for the non-irradiated specimen, $\tau_2^0 = 3.5 \pm 0.2$ ns).[124]

VI. THE FATE OF POSITRONIUM IN IRRADIATED POLYMERS

1. Teflon

The lifetime of orthopositronium τ_2 in PTFE irradiated with ^{60}Co γ-rays is not determined[124] unambiguously by the concentration of free radicals n_s (Fig.11). The rupture of the C–F and C–C bonds leads to the formation, together with free radicals, of vacancies at the sites of fluorine atoms or in the slit arising in the main polymer chain as a consequence of some compression of its two sections after the dissociation of the C–C bond[124]. The positronium located in these vacancies (type A) can be rapidly "quenched" by the neighbouring unpaired electron (lifetime $\tau_2' < \tau_2^0$). Saturation with respect to the yield of radicals is due to their recombination, but the slits at the sites of dissociation of the C–C bonds are retained under these conditions. Such slits again serve as the locations (type B) of Ps atoms, but here positronium is annihilated after a time $\tau_2'' \cong \tau_2^0$. The authors[124] expressed the observed lifetime of orthopositronium by the formula

$$\frac{1}{\tau_2} = \frac{N_0 + N_B}{N_0 + N_A + N_B}\frac{1}{\tau_2^0} + \frac{N_A}{N_0 + N_A + N_B}\frac{1}{\tau_2'}, \qquad (10)$$

where N_0 is the number of vacancies in the non-irradiated polymer and N_A and N_B are the numbers of vacancies of types A and B. The quantities N_A and N_B are related to the dose D, the radiation intensity I, and the radiation yield in the formation of radicals q by the expressions[2]

$$N_A = N_S\frac{\exp(2N_S ID) - 1}{\exp(2N_S ID) + 1}, \quad N_B = qD - N_A,$$

where $N_S = qI/k_r$, k_r being the rate constant for the recombination of radicals. The limiting value is $N_A = N_S$. The maximum value of τ_2 is attained when $N_0 + qD = \frac{1}{2}N_S\exp(2N_S ID)$. On the other hand, if $D \to 0$ or $D \to \infty$, then $\tau_2 \to \tau_2^0$, which is observed experimentally. It should be noted that Eqn.(10) is inconsistent with the "positronium capture model". In essence, it is assumed in Eqn.(10) that the *o*-Ps atom can undergo pick-off annihilation with a probability $1/\tau_2^0$ and quenching by radicals with a probability $1/\tau_2'$.

When the TD spectrum was resolved into three components, and not two as in the study of Chandra et al.[124], Green and Tao[125] observed a decrease of the "longest time" τ_2 and an increase of the ratio $I_1/(I_1 + I_2)$ with increase of the γ-irradiation dose in PTFE. Green and Tao[125] explained the decrease of τ_2, like Chandra et al.[124], by the quenching of positronium by radicals and the increase of the ratio $I_1(I_1 + I_2)$ by the increase of the degree of crystallinity of PTFE (in conformity with the hypothesis of the same workers[89], mentioned above). Later measurements[21,126–128] confirmed on the whole the results of the above studies[124,125] and at the same time revealed the influence of air on the dependence of τ_2 and I_2 on the irradiation dose, but the results were contradictory (cf. for example, the data of Hsu and Hadly[21] and Khan et al.[126]). Furthermore, according to the measurements of Hsu and Hadley[21], the intensity I_1 of the intermediate component is independent of the irradiation dose (in contrast to the data of Green and Tao[125]). If this is so, it would follow, according to Hsu and Hadley[21], that the component τ_1 of TD is not related to the pick-off annihilation of orthopositronium and the problem of its nature arises again (see above).

The influence of γ-irradiation on TD in PTFE has been studied[129,130] in the region of small doses (up to 30 kGr). Together with TD spectra, measurements were made of the EPR and NMR spectra, the density, and the dielectric constant. It was shown that the dependence of the degree of conversion of positronium in irradiated PTFE on the irradiation dose is influenced by factors such as the change in free volume, free radicals, and crystallinity.

2. Polyethylene

In contrast to PTFE, when PE is subjected to γ-irradiation[131], radiation-induced cross-linking of the chains takes place and not their degradation at C–C bonds. For rapid cross-linking, an EPR signal is not observed. According to X-ray diffraction data[131], the irradiation of PE leads to a decrease of the number and size of the polymer microcrystals with a corresponding increase of the fraction of amorphous low-density regions. Therefore, from the standpoint of the "free volume" model, one may expect an increase of the lifetime τ_2 on irradiation of PE, which has indeed been observed (see Fig.12). (The TD spectrum was resolved into two components[131]). Data concerning I_2 were not presented[131].

Ito and Tabata[132] measured TD in PE obtained from ethylene at high pressure by radiation polymerisation. The polymer was irradiated with γ-rays and the TD was measured at −78 °C *in vacuo*. As a result, it was possible to "reveal" the influence of free radicals on the quenching of orthopositronium in PE; there is a linear relation between the increase of the rate of annihilation of orthopositronium λ_2 under irradiation and the increase of the spin concentration n_S, namely $\Delta\lambda_2 = \lambda_2 - \lambda_2^0 = k_r n_S$, where $k_r \cong 0.22 \times 10^{-17}$ m^3 spin^{-1} s^{-1}. With the increase of the irradiation dose, τ_2 decreases linearly, while I_2 remains almost unchanged (approximately 30%). The decrease of τ_2 in γ-irradiated PE (at low temperatures) was explained[132] by the "quenching" of orthopositronium as a result of the reaction of *o*-Ps atoms with free radicals R: $Ps + R \rightarrow PsR \rightarrow 2\gamma$. The rate of this reaction is an order of magnitude lower than the rate of reaction of *o*-Ps atoms with acceptors in solutions. Assuming that the mobility of the *o*-Ps atoms is determined by diffusion, Ito and Tabata estimated the diffusion coefficient of *o*-Ps atoms: $D_p = (0.58-1.75) \times 10^{-9}$ m^{-2} s^{-1}. The value of D_p obtained is higher than for the reaction of *o*-Ps atoms with DPPH in solid pyridine at −78 °C but lower than, for example, for the diffusion of *o*-Ps atoms in metal oxides.

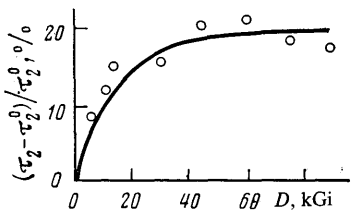


Figure 12. The relative increase of τ_2 in polyethylene with increase of the dose of irradiation by ^{60}Co γ-rays ($\tau_2^0 = 2.0 \pm 0.2$ ns).[131]

3. Polystyrene

Thosar et al.[133] did not observe an influence by γ-radiation (doses up to 250 kGr) on PS—either on τ_2 or on I_2. However, the results of Hsu and Hadley[134] led to the opposite finding. They investigated very dense PS specimens with a low crystallinity, obtained from the monomer by annealing *in vacuo* at 70 °C. The PS specimens were irradiated with ^{137}Cs γ-rays (dose rate 10^3 Gr h^{-1}). The irradiation and the measurement of TD were carried out at room temperature *in vacuo* and in air.

Vacuum irradiation (dose 80 kGr) leads to a decrease of I_2 from approximately 33.8% to approximately 29.3% when TD is measured *in vacuo*; after annealing the irradiated specimens at 70 °C for 24 h and measurement of TD under the same conditions, the previous value of I_2 is found to be restored (approximately 33.5%); on the other hand, measurement in air yields $I_2 \cong 30.4\%$. In air I_2 decreases with increasing irradiation dose from approximately 34.1% to approximately 28.2% for a dose of 150 kGr; τ_2 also diminishes somewhat under these conditions (from 2.33 ± 0.02 to 2.25 ± 0.02 ns). After annealing, the previous value of I_2 is restored, while τ_2 remains unchanged (or decreases slightly: $\tau_2 = 2.23 \pm 0.02$ ns). The changes in I_2 are apparently due to the inhibition of the formation of positronium in γ-irradiated PS by free radicals and also by stable oxygen-containing groups (C=O and OH)—the products of the conversion of free radicals in the presence of atmospheric oxygen[134]. The insensitivity of τ_2 to γ-irradiation is explained by the absence of appreciable changes in the supermolecular structure (i.e. in the "free volume").

Irradiation of PS with neutrons in the thermal column of a nuclear reactor causes a marked decrease of I_2 (by approximately 40% for a dose of approximately 2.4×10^7 kGr), leaving $\tau_2 = 2.2 \pm 0.2$ ns unchanged[133]. Neutron irradiation of PS leads to the breakdown of the benzene rings (according to NMR data) and to the accumulation of free radicals (according to EPR data). Since the formation of positronium in PS is probably associated mainly with benzene rings[133], the breakdown of the latter under neutron irradiation leads to a decrease of I_2. Hence, if Ps atoms are annihilated preferentially in the benzene rings, the quenching influence of the free radicals produced under irradiation outside the benzene rings will be negligible compared with the quenching of the Ps atoms as a consequence of pick-off annihilation by interaction with the electrons of the aromatic rings.

The results of the study of the influence of irradiation on the formation and destruction of positronium in polymers (as in other molecular substances[2] and even in substances such as quartz[10,92]) confirm qualitatively the "free volume" model and the role of order. At the same time it has been observed that in molecular solids (apart from the studies quoted above, see also, for example, Refs. 1, 15, 110, 111, and 135–139), the quenching of positronium by free radicals can play a significant role together with pick-off annihilation. The same conclusion follows also from the analysis of the measurements of the TD and AD parameters in polymers subjected to thermal degradation, which was already mentioned above. One should note that an estimate[111] of the rate of quenching of positronium by radicals in PVC yielded a value greater by 3–4 orders of magnitude than that observed in PE (see above): $k_r \cong 8.4 \times 10^{-12}$ kg spin^{-1} s^{-1}. Free radicals (as well as their reaction products) can apparently function not only as quenching agents but also as inhibitors of the formation of positronium.

4. The Quenching of Positronium by Radicals

The mechanisms of the quenching of positronium by free radicals (or stable groups—the products of the reactions of radicals) can be various: *ortho–para* conversion, addition and oxidation reactions, etc. Analysis of the kinetics of the reactions of positronium taking into account the above quenching mechanisms shows that the increase of the rate of quenching of orthopositronium is

$$\Delta\lambda_2 = \lambda_2 - \lambda_2^0 = k = k_r n_s, \qquad (11)$$

where $\lambda_2^0 = \lambda_t^0 + \lambda_p$ and k is the rate constant of *ortho–para* conversion, the addition reaction, the oxidation reaction, etc. In the case of *ortho–para* conversion Eqn. (11) is valid provided that $k \ll \lambda_S^0$ and $\lambda_p \ll \lambda_S^0$. In terms of the approximation indicated, *ortho–para* conversion leaves unaltered the intensity of the long-lived TD component ($I_2 \cong \frac{3}{4}P$) and intensifies the narrow AD component:

$$I_N \simeq \frac{1}{4} P \left(1 + \frac{3k}{\lambda_2^0 + k}\right).$$

As already mentioned, in γ-irradiated PE the intensity I_2 remains almost unchanged as λ_2 increases [in conformity with Eqn. (11)] in the course of the accumulation of free radicals[132].

The addition reaction $Ps + R \rightarrow PsR$ weakens both the long-lived TD component, i.e.

$$I_2 = \frac{3}{4}P\left(1 - \frac{k}{\lambda_p + k + \lambda_{pr}}\right),$$

where λ_{pr} is the rate of pick-off annihilation in the PsR system, and the narrow TD component:

$$I_N \simeq \frac{1}{4}P\left(1 - \frac{k}{\lambda_s^0}\right) \text{ (for } \lambda_p, \lambda_{pr}, k \ll \lambda_s^0).$$

One cannot rule out the possibility that the simultaneous decrease of τ_2 and I_2 (in terms of our notation!) on γ-irradiation of PS is due to the addition reaction[134].

In the oxidation reaction $Ps + R \rightarrow Re^- + e^+$ the I_2 and I_N components are also simultaneously weakened [for example, $I_N \cong \frac{1}{4}P(1-\frac{\lambda_p + k}{\lambda_s^0})$], but, in contrast to the addition reaction, other TD parameters behave differently.

Each version of the quenching of positronium by radicals thus has its specific distinctive features, which make it possible to identify them from experimental data. Other mechanisms of the quenching of positronium by radicals examined above behave analogously. It is easy to see also the possible ways of devising general models taking into account the "free volume" and "positronium capture" models. In order to construct general models taking into account the possibility of the limitation of the rates of reaction by the rate of diffusion of Ps atoms and radicals (as well as traps), one can use the formal treatment developed by Brandt, Seeger, and coworkers[52-56].

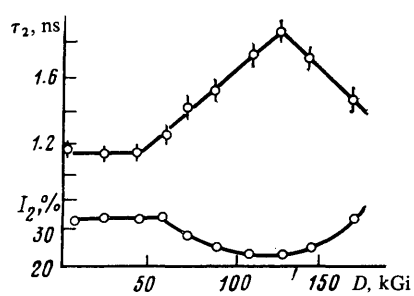


Figure 13. Dependence of τ_2 and I_2 on the irradiation dose for the crystalline monomer *N*-vinylcarbazole (rate of irradiation 7.2×10^{-2} Gi h^{-1}).[136]

VII. THE EFFECTS OF THE MOLECULAR WEIGHT AND COMPOSITION

1. The Effects of the Molecular Weight

In the radical polymerisation of *N*-vinylcarbazole ($C_{15}H_{14}N$), a crystalline monomer, the TD parameters (τ_2 and I_2) associated with orthopositronium depend in a complex manner on the degree of polymerisation[136] (Fig.13). The maximum in τ_2 corresponds to the polymerisation saturation point; further irradiation leads to the accumulation of positronium quenching radicals, which is the reason, according to the authors[136], for the decrease of τ_2 in the region of doses ≥130 kGr. Analogous studies were carried out also for other monomers[1,140-143], but their results showed that the parameters of the TD spectrum are sensitive to the degree of polymerisation and are correlated with EPR data.

Khan[111] studied in detail the influence of temperature on τ_2 (and also on I_2) in PVC, which differs from the polymers studied in most of the investigations quoted above by being thermally unstable. Measurements were made of the long lifetime τ_2, of the intensity of the EPR signal (concentration of free radicals), and of the decrease of the molecular weight as a function of the time *t* during which specimens of pure and plasticised PVC with different initial molecular weights were heated at a constant temperature (at 150 °C and also, for comparison, at 170 °C). Findings such as the exponential decrease of τ_2 with increase of the duration of heat treatment (the ratio $\tau_2/\tau_2^0 \cong 0.2$ for $t = 7$ days) together with the exponential increase of the concentration of free radicals and decrease of the molecular weight, and the dependence of the rates of the above changes on the molecular weight, temperature, etc. show that the quenching of positronium is due to the free radicals arising in the thermal degradation of PVC.

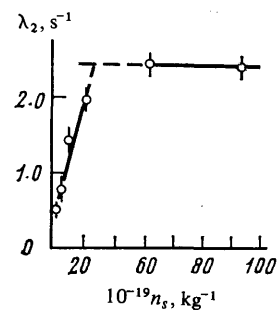


Figure 14. Dependence of $\lambda_2 = \tau_2^{-1}$ on the concentration of free radicals n_S produced by thermal degradation at 150 °C in pure poly(vinyl chloride) powder with $M = 200000$.[111]

Khan believes that positronium is more likely to be quenched by the capture of Ps atoms by free radicals (addition) or the capture of the unpaired electron of the free radical by a Ps atom with formation of the Ps^- ion (formally this mechanism can be regarded as an addition reaction—Section VI) and not via the *ortho–para* conversion mechanism. Evidence in support of the formation of the ion comes from the finding that τ_2 in PVC reaches a minimum value (0.37 ± 0.05 ns) at a spin concentration $n_S \cong 25 \times 10^{19}$ spins kg^{-1} and remains unchanged as n_S increases further (Fig.14). The minimum value of τ_2 is almost equal to the lifetime of the ion Ps in relation to annihilation (0.35 ns).

The dependence of the lifetime of positrons on the average molecular weight M_w has been observed directly[144,145] for polypropylene. The following approximate relation holds for the TD components:

$$\tau_i = \tau_i^0 - \delta_i \bar{M}_w,$$

where τ_i^0 and δi are constants. For polypropylene, $\tau_0(\text{ns}) = 0.30 - 0.080 \times 10^{-6}\,\bar{M}w$ and $\tau_2(\text{ns}) = 0.48 \times 10^{-6}\,Mw$. Chuang and

Tao[145] attempted to justify this relation in terms of the "free volume" model.

2. Elastomers

Interesting results have been obtained[7,146-148] from measurements of the parameters τ_2, I_2 and $P_{3\gamma}$, characterising the probability of the formation and quenching of positronium in elastomers. On passing from raw rubber to isoprene and then to cured rubber (3% of sulphur), a decrease is observed in $P_{3\gamma}$ (the ratio $P_{3\gamma}/P^0_{3\gamma} = 3.8$, 2.08, and 2.2 respectively) and I_2 (50, 13, and 26% respectively), while $\tau_2 \cong 2.2$ ns remains almost unchanged. On passing to ebonite (32% of sulphur) and to sulphur, τ_2 falls to approximately 0.5–0.6 ns. A more detailed study of the AD and TD parameters (I_N, I_2, and τ_2) for raw rubber and its vulcanised forms with different sulphur contents (up to 10%) and corresponding to different vulcanisation times confirmed the decrease of I_2 [under these conditions, $\Delta I_2 \cong 3\Delta I_N$; see Eqn.(5)] with increase of the sulphur content, I_2 being proportional to the degree of unsaturation. With increase of the vulcanisation time, ΔI_2 increases in parallel with the increase of the relative amount of bound sulphur.

A correlation between the network density and the change in I_2 (at $t = 40$ min, I_2 diminishes by a factor of approximately 2) has been observed[15,84] for sulphur-vulcanised ternary ethylene–propene rubber with increase of the vulcanisation time.

The observed decrease of I_2 from 28% for raw rubber to 8% for raw rubber +10% S, to which corresponds a weakening of the narrow component in AD ($\Delta I_2 \cong 3\Delta I_N$) with a virtually unchanged τ_2 has been attributed[146] to the inhibition of the formation of positronium with decrease of the degree of unsaturation, i.e. of the fraction of double bonds in the rubber (it varies from 95 to 74% respectively). On the other hand, the relation $\Delta I_2 \cong 3\Delta I_N$ indicates the absence of chemical interactions between the Ps atoms and the surrounding molecules and groups and of *ortho–para* conversion (see Section VI, subsection 4). It is suggested that positronium is formed in raw rubber at the sites of double bonds as a result of the capture of π-electrons by positrons. The formation of positronium is apparently inhibited as a result of the annihilation of the volumes in which it can be formed and exist (by analogy with the influence of the neutron irradiation of PS on I_2—see above). The inhibiting effect of the non-static (microheterogeneous) distribution of vulcanisation cross-links on the formation of positronium in raw rubber relative to the static (homogeneous) distribution has been observed[148].

Having applied the "positronium capture" model (see Section III, subsection 3), Arifov et al.[148] estimated from TD parameters the probability P of the formation of positronium and the rate constant k for its capture by traps in elastomers based on the butadiene–styrene rubber: $P \cong 0.6$–0.7 and $k \cong (0.6\text{–}0.7) \times 10^9$ s^{-1}. The extent of the region (trap) in which the Ps atom is localised in the rubber amounts to approximately 0.86 nm, which corresponds to the distance between the groups of neighbouring chains[51,146].

3. Mixtures

Studies have been made[1] on mechanical mixtures of PVC and PE homopolymers and graphite–polyethylene and graphite–4-vinylpyridine copolymers. In the case of macromixtures (grain size more than 10 nm) the annihilation characteristics of the mixture constitute a linear superposition of the annihilation characteristics of the initial polymers; in micromixtures there is no such superposition. It is assumed that in macromixtures positronium is localised in the component where it was formed, while in micromixtures, it is able to diffuse into the other mixture component. The influence of the micromixture on the reactions of positrons and positronium in filled polymers (PE + Al_2O_3 + perlite, polybutadiene + carbon black, etc.) has been investigated[15,86,91,149]. In the case of filled PE it proved possible to elucidate[15,91] the cause of the strengthening of the material (maximum degree of crystallinity) for a specific content of the filler (35%) and also the role of pressure and temperature in the treatment of the material.

Here we shall also point to studies[150-152] in which measurements were made of TD (and AD) in mixed organic crystals and to an investigation[81] in which it was noted that, according to the TD measurements, the vitrification of dry nylon occurs at 50 °C, while in the presence of 0.5% of water it takes place at 30 °C, which indicates yet again a fairly considerable sensitivity of the positron method. There is no theory of the formation and reactions of the positrons and positronium in polymers of complex composition, in elastomers, and in mixtures and compositions.

VIII. THE INFLUENCE OF THE ELECTRIC AND MAGNETIC FIELDS ON THE REACTIONS OF POSITRONS AND POSITRONIUM IN POLYMERS

1. The Effects of the Electric Field

The formation of positronium in matter in the presence of an electric field has been studied theoretically[71,153-155]. On the one hand, the field displaces positrons outside the limits of the Ore gap (see Section III), which leads to a decrease of the probability of the formation of positronium, and, on the other hand, the heating of "slow positrons" increases the yield of positronium. The relative contributions of the two processes are determined by the ratios of the cross-sections for the positronium processes, the loss of energy by positrons, and the annihilation of positrons. In weak fields the first of the above effects of the electric field may predominate the inhibition of the formation of positronium may therefore be observed (see also the considerations put forward by Mogensen[156]). The effect involving the "heating" of positrons by the field, i.e. the increase of the yield of positronium, predominates in strong fields. Experiments with gases on the whole confirmed this picture[2,154,155].

On passing to polymers, we note in the first place that in polymers the probability of the formation of positronium as well as the rate of its quenching depend appreciably on the dipole moment of the molecules: I_2, τ_2, and $P_{3\gamma}$ decrease with increase of the molecular dipole moment of the polymer (see, for example, Refs.7, 89, and 157). For example, the above quantities have the following values for PE and PVC with almost identical valence-electron densities and ionisation potentials but markedly different molecular dipole moments (0 for PE and 6.7×10^{-3} C m for PVC):[7] $P_{3\gamma} = (2.14 \pm 0.3) P^0_{3\gamma}$, $I_2 = 22 \pm 2\%$, and $\tau_2 = 2.1 \pm 0.2$ ns for PE; $P_{3\gamma} = (1.23 \pm 0.15) P^0_{3\gamma}$, $I_2 = 13 \pm 2\%$, and $\tau_2 = 1.23 \pm 0.1$ ns for PVC.

Thus in polymers and, incidentally, in liquids[2] the probability of the formation of positronium diminishes with enhancement of the polarity, i.e. with increase of the molecular dipole moment, while the rate of pick-off annihilation actually increases. The effect of polarity is shown clearly on passing from raw rubbers (non-polar compounds) to isoprene (in which the C–CH_3 bond leads to a dipole moment

of 1.7×10^{-30} C m), cured rubber, and ebonite (32% of sulphur) (polar dielectrics)[7] and from butadiene–styrene rubber with a static (homogeneous) distribution of vulcanisation cross-links to a rubber with a non-statistical (heterogeneous) distribution of such links[140].

The electric field of the dipoles can apparently influence not only the probability of the formation of positronium but also the spatial distribution of positrons and positronium in matter, directing them (positrons and Ps atoms) to specific atomic groups (into the region of enhanced electron density), so that their annihilation is accelerated. Furthermore, the rate of self-annihilation and the half-width of the momentum distribution of Ps atoms can change significantly in the electric field of the dipoles[158].

Static fields up to $E = 12$ MV m^{-1} decrease significantly the lifetime of the long-lived component in PTFE and PE: $\tau_2 = \tau_2^0(1-\alpha E)$, where $\alpha = (9.3\pm1.3)\times10^{-3}$ m MV^{-1}, while in polar polymers (lucite, nylon, and PVC) this type of influence of the field has not been observed[74]. The absence of an effect by the electric field on τ_2 in polar polymers is apparently associated with the fact that in the vicinity of the electric dipoles generated by them the field greatly exceeds the external field.

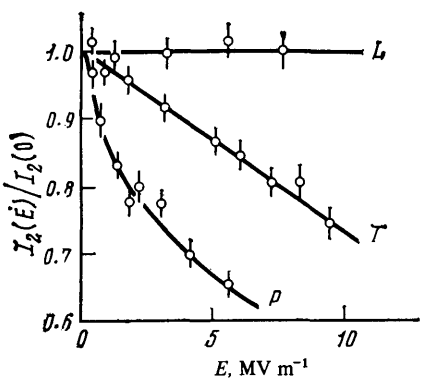


Figure 15. The influence of the electric field on the intensity of the long-lived TD component (τ_2) in lucite (L), Teflon (T), and polyethylene (P).[159]

In typically non-polar polymers like PS and PTFE the probability of the formation of positronium greatly diminishes with increase of the electric field (by 33 and 13% respectively for $E = 5$ MV m^{-1}). On the other hand, in polar polymers (lucite, nylon, and PVC) the electric field does not affect the probability of the formation of positronium (Fig.15)[159] (this may be due to the cause indicated above in the discussion of τ_2). Analogous conclusions were also reached on the basis of the analysis of the results of measurement of $P_{3\gamma}$ in polymers with application of a static electric field: $P_{3\gamma}(E) = P_{3\gamma}(0)(1-\beta E)$ for non-polar polymers, where $\beta \approx 0.80$ m MV^{-1} for PS and $\beta \approx 0.022$ m MV^{-1} for PTFE.[7] The influence of the electric field for PTFE and PE has also been investigated in other studies[71,160-166]. We may note that the results quoted by Patterson and Stewart[160] conflict with the previous ones: no effect of the field (on AD) is not observed up to 11 MV m^{-1}. The absence of a field effect in polar polymers has been confirmed[71].

Bertolaccini et al.[164] (see also Refs.162 and 163) observed a time effect in the influence of the electric field on the probability of the formation of positronium in PE. Immediately after the application of the field, $P(E)$ decreases sharply relative to $P(0)$ and then, when some time has elapsed, the ratio $P(E)/P(0)$ begins to increase and reaches a plateau (Fig.16). On the other hand, in the initial instant the probability of the formation of positronium in PE decreases with increasing field, in conformity with the results of previous measurements. When the field has been switched off, the ratio $P(E)/P(0)$ does not immediately reach unity (Fig.17). It has been suggested[164] that the time dependence of the probability of the formation of positronium in PE, observed when the field is applied and removed, is a consequence of the relaxation of the effective electric field $E(t)$, which in fact acts upon the PS atom in the given substance. The data in Figs.16 and 17 agree with the $E(t)$ relation of the type $E(t) = E(\infty) + [E(0)-E(\infty)]\exp(-t/\tau)$. Thus a whole series of effects of the electric field have been observed in polymers: the effect of the polarity of the polymers, the quenching and inhibition of the formation of positronium, and relaxation effects in the inhibition of the formation of positronium by the electric field.

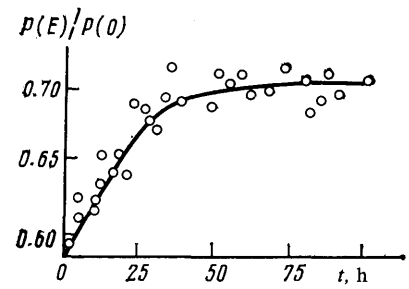


Figure 16. Dependence of the probability of the formation of positronium in polyethylene on the time elapsed from the instant of the application of the electric field $E = 10$ MV m^{-1}.[164]

2. Magnetic Quenching of Positronium in Polymers

The magnetic field (B) is one of the most reliable indicators for the determination of the amount of positronium formed in a given substance. The observed quenching of positronium by the magnetic field constitutes an additional source of information about the properties of positronium in the given substance and hence about the properties of the substance itself.

In the simplest case where the interaction of positronium with the surrounding medium reduces to pick-off annihilation (see Section III), the factors characterising the changes in $P_{3\gamma}$, I_N, and I_2 in a magnetic field as a consequence of the magnetic quenching of positronium are given by the following expressions (see, for example, Refs.2, 12, 33,47, and 167–170) in terms of the approximation $y^2 \ll 1$ [$y = [(1+x_2)^{1/2}-1]/x$, where $x = 4\mu_B B/\Delta E$, μ_B = Bohr magneton, and ΔE is the amount by which the energy of the triplet substate of the Ps atoms exceeds the energy of the singlet substate; *in vacuo* $\Delta E = 8.4\times10^{-4}$ eV], which is valid for

$\lambda_p \ll \lambda_s^0$ and fields up to $B = 2$ Tl:

$$w_{s\gamma} = P_{s\gamma}(B)/P_{s\gamma}(0) = 2/3 + 1/3(1-Q)^{-1}, \quad (12)$$

$$\varepsilon(B) = [I_N(B) - I_N(0)]/I_N(0) = Q/(1+Q), \quad (13)$$

$$R(B) = \left[\int_{\tau_2}^{\infty} p(t)\,dt\right]_B \Big/ \left[\int_{\tau_2}^{\infty} p(t)\,dt\right]_0 = \frac{1}{3}(2 + e^{-Q}), \quad (14)$$

where $Q = y^2\tau_2/\tau_s^0$ is the parameter of the magnetic quenching of positronium. In still weaker fields, where $x^2 \ll 1$ ($x = 0.275$ V if B is expressed in Tl), one can put $Q \approx 0.151\,B^2\tau_2$ (B expressed in Tl and τ_2 expressed in ns).

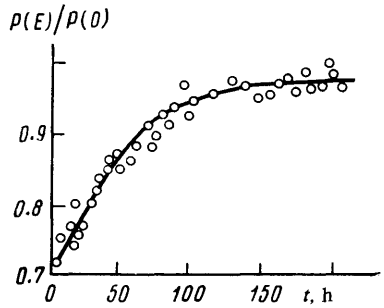


Figure 17. The relaxation of the formation of positronium in polyethylene after switching on the electric field $E = 10$ MV m^{-1}.[164]

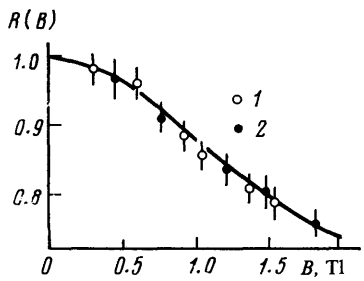


Figure 18. Suppression of the long-lived TD component by the magnetic field in Teflon (*1*) and lucite (*2*); circles—experimental data; lines—calculated data[167].

The nature of the influence of the magnetic field on the experimental characteristics of the annihilation of positronium in matter can be seen directly from Eqns.(12)–(14): in the presence of a magnetic field the probability of 3γ-annihilation [Eqn.(12)] diminishes, the narrow AD component intensifies [Eqn.(13)], and the long-lived component τ_2 of the TD spectrum is suppressed [Eqn.(14)]. The results of the observation of the magnetic quenching of positronium in polymers[2,33,47,167,169,171–177] confirmed the theoretical conclusions (Fig.18). The magnetic quenching of positronium has been investigated[178] within the framework of the "positronium capture" model.

Having analysed the results of the measurements of the factor $R(B)$ in PTFE, PE, PS, PVC, and nylon, Bertolaccini et al.[177] concluded that the Ps atom is "deformed" in polymers (as in ionic crystals[12]). The deformation of the Ps atom in matter can be characterised by the relation $\alpha_m = |\psi(0)|m^2/|\psi(0)|_0^2$, where $|\psi(0)|m^2$ and $|\psi(0)|_0^2$ is the electron density at the "zero" point in the Ps atom in matter and *in vacuo*. In polymers $\alpha_m \leq 1$ (Table 4), i.e. the Ps atom exhibits a tendency to "swell"[177]. Within the framework of the phenomenological model of the interaction of positronium with the surrounding medium, proposed by Urbanovich[179], the energy of the interaction of the atom with the molecules surrounding it in a given substance can be estimated, provided that the parameter α_m is known: $U(\text{eV}) = -13.6(1-\alpha_m^{1/3})^2$. As was to be expected, in polar polymers (PVC and nylon) the interaction of the Ps atom with molecules is stronger than in non-polar polymers (Table 4).

Table 4. The "deformation" parameters (α_m) and the energies U of the interaction of the Ps atom with the surrounding medium in polymers.

Substance	α_m (Ref.162)	$-U$, eV
Teflon	1.00±0.09	0
Polyethylene	0.71±0.04	0.16
Polystyrene	0.80±0.06	0.07
Poly(vinyl chloride)	0.060±0.08	0.35
Nylon	0.56±0.4	0.44

The influence of the magnetic field on the intermediate TD component τ_1 in different polymers is manifested unequally[177]: in PTFE no effect of the field is observed, in PE, PS, and nylon the effect is very weak, and in PVC the magnetic quenching of the component τ_1 is clearly observed. It can therefore be suggested (see Section V) that the component τ_1 is due to the positron state which is to some extent positronium-like. One should note that there are still comparatively few data concerning the influence of fields on the AD and TD parameters and $P_{3\gamma}$ and the available data are frequently fragmentary. Such data are necessary to refine our ideas concerning the mechanisms of the reactions of positrons and positronium in polymers and, as already mentioned, to convert "qualitative" information, provided by the method indicated, into quantitative information.

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Fairly extensive experimental data have now accumulated on the properties of positrons and positronium in polymers and we are able to account for the results of the measurements at least qualitatively if not quantitatively. The available data make it possible to claim confidently that positrons effectively "sense" polymers and therefore the positron method can indeed become a valuable supplement to the already existing methods in the physics and chemistry of polymers. Naturally much is still obscure and even contradictory in both experimental results and in their interpretation. There are virtually no data obtained simultaneously by all methods for the observation of the annihilation of positrons (AD, TD, AD-TD, $P_{3\gamma}$, etc.) in the same specimens with

a well known history. There is no rigorous quantitative theory of many of the observed phenomena. Nevertheless studies are being performed along a widening front, the number of investigators is increasing, the experimental technique and methods are being improved, and theoretical studies are being prosecuted; it may be hoped that the positron method will permit the solution of many problems in the physics and chemistry of polymers and other substances[180].

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Catalytic Properties of Zeolites Towards Oxidation Reactions

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We shall review experimental data on the catalytic properties of zeolites towards the oxidation and oxidative dehydrogenation of aliphatic, naphthene, and alkylaromatic hydrocarbons, and of inorganic or organic molecules containing hetero-atoms. The influence of the zeolite structure, of the nature and concentration of the exchangeable cations, and of the valency state of the transition metals on the activity and selectivity of the catalysts will be discussed, together with the effect of these factors on the course of the hydrocarbon oxidation reactions. Specific aspects of the interaction of molecular oxygen and of oxidisable compounds with various zeolites will be examined in the light of ESR, i.r. spectroscopy, and thermal desorption data. We shall show that variations in the structure and composition of the zeolite can lead to different types of reaction, yielding valuable products, and thus confirming the importance of zeolites among oxidation catalysts. 188 references.

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I. INTRODUCTION

Zeolites are salts of solid alumino-silicic acids, characterised by a well defined crystal lattice structure and classified as catalysts of the acidic type. Since the earliest reports of the high catalytic activity of zeolites[1-3] a great deal of work has been done on the acidic properties of zeolites and on their catalytic activity towards reactions of the acid–base type (cracking, isomerisation, alkylation, etc.). Efficient bifunctional catalysts have been developed from zeolites containing Group VIII metals.

One of the least characterised of the zeolite-catalysed reactions of hydrocarbons is their oxidative transformation. The problem is inadequately discussed in the reviews and monographs on zeolites which have been published so far[4-22], and therefore the present review will attempt to deal with various problems in the oxidation of aliphatic, naphthene, and alkylaromatic hydrocarbons, and of H_2, CO, NH_3, H_2S, and alcohols in the presence of zeolites of different composition and structure.

II. OXIDATION OF ALIPHATIC HYDROCARBONS

Though the oxidation of ethylene[23] and of H_2S [24] on zeolites was first reported in 1961, detailed studies of these reactions began only more recently. The deep oxidation†

†This term is used throughout the paper to denote total oxidation to CO_2 and H_2O.

of methane on type X zeolites containing various transition metal cations has been investigated[25,26], and the reaction on iridium-, rhodium-, and palladium-containing zeolites has been shown to be kinetically of first order with respect to methane and of zero order with respect to oxygen[25]. On a Pt-containing X-type zeolite the reaction has a negative order with respect to oxygen, suggesting competitive adsorption of methane and oxygen. The correlation between the activity of the zeolite and the coordination number of the transition metal cation has been stressed[26]. The activation energy of the reaction on Pd-containing type X zeolites prepared by steeping and by ion exchange methods is 50 and 88 kcal $mole^{-1}$ respectively, indicating a large difference in the catalytic properties towards the deep oxidation of methane between metallic palladium and the palladium cations in a zeolite lattice.

The oxidation of ethylene on type Y zeolite containing transition metal cations is discussed in Refs. 27 and 28. Deep oxidation of ethylene, with formation of CO_2 and H_2O, was observed on all the samples. The most active catalysts are Cu(II)Y and Cr(III)Y, and the least active are Ni(II)Y and Mn(II)Y, the latter being almost indistinguishable from the initial NaY zeolite in catalytic activity. The possibility of participation in the reaction by the oxygen atoms of the catalysts themselves was tested by first treating the zeolites with oxygen and then admitting the ethylene as a series of separate pulses. The presence of active oxygen in the zeolite is inferred from the appearance of peaks of reaction products in the chromatograms. The amount of reaction oxygen stored in the sample depends on the nature of the ion-exchange cation. With the least active [Ni(II)Y and Mn(II)Y] samples the amount of oxidation products detected in the chromatograms is very small, whereas on Cu(II)Y zeolite the amount of active oxygen increases steeply with the oxygen pre-treatment temperature.

The catalytic activity of type Y zeolite and the amount of reactive oxygen held by the catalyst have been shown[29] to vary non-linearly with the degree of exchange of sodium by copper cations, suggesting non-equivalence of the copper localisation sites in the zeolite lattice. Activated adsorption of ethylene in the pre-catalytic region has been demonstrated. At lower temperatures physisorption takes place, and the degree of exchange of sodium by copper ions has no effect on the heat of adsorption of ethylene. After removal of the active oxygen from CuY zeolites the adsorption of ethylene is markedly enhanced, possibly as a result of a strong direct bond between ethylene and the copper ion. Substantial adsorption of ethylene on Cu(I)Y and Ag(I)Y zeolites with formation of π-complexes has been detected[30] by i.r. spectroscopy. With the Cu(II)Y, Zn(II)Y, and CaY zeolites the main contribution to the interaction with ethylene is from van der Waals forces. The heat of adsorption of ethylene on Cu(I)Y is 15.9 kcal $mole^{-1}$, but only 9.5 kcal $mole^{-1}$ on Cu(II)Y.

An oxidation reaction of ethylene of great practical importance is the preparation of ethylene oxide. A method of producing ethylene oxide by using zeolite catalysts was patented[23] in 1961, but a detailed study of this reaction on type A and X zeolites in the presence of ionic silver was only recently reported[31]. Samples prepared by ion exchange were shown to have a low selectivity towards ethylene oxide at 200–300 °C, whereas the catalysts prepared by steeping the initial zeolite offer both a high activity and a high selectivity in this reaction. The most selective catalyst is Ag–CaA, the yield of ethylene oxide and the selectivity of the reaction increasing in proportion to the amount of silver and reaching levels of 25 and 70% respectively on a 30% Ag–CaA catalyst at 250 °C.

The oxidation of ethylene on type Y zeolite containing both copper and palladium cations has been shown[32–35] to give acetaldehyde in the presence of water vapour. In isolation, neither Pd(II)Y nor Cu(II)Y is an active catalyst; the activity of a sample prepared by adding first 4 wt.% of Cu and then 1 wt.% of Pd is twice as high as that of a catalyst containing the same amounts of Cu and Pd but added in the reverse order[32].

The activity of PdCu catalysts towards the oxidation of ethylene and propylene is markedly dependent on the crystal structure of the zeolite[33]. In particular, the X and Y zeolites with large pores are more active towards the formation of acetaldehyde than type A and mordenite type zeolites. It appears that the reaction takes place mainly in the zeolite lattice holes, and the contribution to the total activity from centres located on the outer surface of the crystal is small. It is stressed[33] that samples prepared by steeping are often superior to ion-exchanged forms of zeolite in both activity and selectivity.

The highest activity towards the oxidation of ethylene to acetaldehyde is found[34,35] in type Y zeolite containing 6 wt.% of copper and 1.5 wt.% of palladium. The optimum oxidative regeneration temperature of these samples was found to be 300°.

Several workers[36–42] have studied the oxidation of propylene on zeolites containing exchangeable transition metal cations. In the presence of type Y zeolite in which the sodium cations have been replaced by copper the main reaction at 350° is deep oxidation of propylene[36]. Small amounts of formaldehyde, acrolein, and acetaldehyde are also formed. A comparison of the activity of Cu(II)Y with that of CuO supported on SiO_2 has shown that the rate of oxidation of propylene on the zeolite can be an order of magnitude greater than on CuO/SiO_2: according to Mochida and coworkers[36] this is due to a specific state of the copper ions on the surface of crystalline aluminosilicates. The activity of Cu(II)Y towards the oxidation of propylene was found to be greater than towards the oxidation of ethylene.

The oxidation of propylene in the presence of water vapour at 300° gives a high yield of acrolein [up to ~7% on Cu(II)Y zeolite if the reaction mixture contains 30–50 vol.% of water vapour[37]]. On Ag(I)Y zeolite under otherwise similar conditions the yield of acrolein is less than 3%, and on Ni(II)Y no acrolein can be detected in general. At 200° isopropanol formation is detected, in keeping with the acidic function of the zeolite.

Increasing the $C_3H_6:O_2:H_2O$ molar ratio in the reaction mixture to 1:1:20 gives acetaldehyde at 250° and acetone at temperatures above 500°.[38] It is pointed out[39] that in order to obtain equal concentrations of acrolein and carbon dioxide in the reaction products the $C_3H_6:O_2$ ratio must be increased to 1:7, and the temperature must be raised to 350°.

In the liquid phase propylene dissolved in benzene is converted into propylene oxide with a selectivity of 70% in the presence of NaX zeolite steeped in ammonium molybdate and of oxygen (150 °C, 45 atm).[40] In a study[41] of the oxidation of propylene on type X zeolites containing Pd, Cu, Co, Ni, Zn, Mn, Cr, Fe, and NH_4 cations the main reaction products were found to be CO_2 and H_2O, with small amounts of acrolein, formaldehyde, and acetaldehyde. The activity of the samples increased with their acidity, but the addition of pyridine to the reaction mixture lowered the activity of the catalysts. From these results the authors concluded[41] that the reaction mechanism is

$$CH_3{-}CH{=}CH_2 + H^+ \rightarrow CH_3{-}C^+H{-}CH_3$$
$$CH_3{-}C^+H{-}CH_3 + (Cu\ldots O_2)^+ \rightarrow CH_3{-}C^+H{-}CHO + H_2O + Cu^+$$
$$CH_3{-}C^+H{-}CHO \rightarrow CH_2{=}CH{-}CHO + H^+ .$$

The intermediate products are further oxidised with formation of CO_2 and H_2O.

Iron-containing zeolites of types A, X, and Y also are active exclusively towards the deep oxidation of propylene[42]. The addition of Fe(III) to X and Y zeolites increases their activity slightly, but in type A zeolite the effect is not detected.

The oxidation of propylene on VONaY zeolite, prepared by ion exchange between NaY zeolite and an aqueous solution of vanadyl sulphate, gives mainly CO_2, acetone, and acetaldehyde[43]. Supported catalysts (V_2O_3/SiO_2) are less active than VONaY towards the oxidation of propylene. It is suggested[43] that this reaction gives only partial oxidation, whose products undergo polymerisation or carbonisation and remain in the internal cavities of the zeolite structure.

The addition of ammonia to the reaction mixture used in the oxidation of propylene leads to oxidative ammonolysis, with formation of acrylonitrile. The activity of the catalysts depends on the structure of the zeolite and on the coordination of the transition metal ions in the zeolite matrix. A study[44] of the activity of Fe(III)-containing zeolites towards this reaction has shown that the yield of acrylonitrile decreases in the sequence FeNaX > FeNaY > FeNaA. The low activity of type A zeolite as compared with the faujasites obviously stems from special features of this type of zeolite skeleton. The most selective catalysts with respect to the formation of acrylonitrile are FeNaX, FeCaX, and FeCaA, whereas FeNaY is the most active towards the formation of CO_2.

The oxidative ammonolysis of propylene has been studied[45] on Fe(II)Y and Fe(II)-mordenite zeolites. At 450° the conversion of propylene on Fe(II)Y was only 17% (10% CO_2, 7% acrolein, acrylonitrile not detected), but in the presence of the Fe(II)-mordenite catalyst the yield of acrylonitrile is as high as 40% for a total conversion of 43%. These results illustrate the important effect of the zeolite structure on the activity and selectivity of the catalyst. Using γ-resonance spectroscopy data Garter and coworkers[45] ascribe this difference between the Fe forms of type Y and mordenite zeolites to the oxidation state and to the location of the iron ions in the two materials.

In the oxidative ammonolysis of propylene and of the butylenes the Mn form of type X zeolite shows a selectivity higher than those of MnY and Mn-erionite zeolites[46], which are more effective as cracking catalysts. It has been pointed out[47] that on NaX zeolite containing 10% Ag_2O the yield of acrylonitrile is 35.5%, whereas gumbrin containing the same amount of silver is more active and selective towards the formation of acrolein.

The interaction of butenes adsorbed on CaA and NaX zeolites with oxygen at 25–90° has been studied[48]. The resulting complex mixture of products can be separated from the zeolites only by extraction with moist ether. This very strong interaction between the zeolites and organic molecules is due to the similarity between the pore size and the molecular diameters. The effect is most clearly seen when the products are more polar than the initial hydrocarbons. After analysing the reaction products the authors[48] conclude that catalytic oxidation on zeolites causes preferential breaking of the double bond.

The Pt–NaA zeolite was found[49,50] to have a high activity towards the oxidation of CO. When a mixture of air and CO (2 mole %) is passed through the catalyst at 427–540° the degree of conversion of CO is 86–100%. Under the same conditions the conversion of n-butane is only 2.4–5.5%.[49] The Pt–CaA zeolite containing 0.3 wt.% Pt has a high selectivity towards the oxidation of n-paraffins and n-olefins mixed with iso-paraffins and iso-olefins. Thus, 97% of the n-butane and only 0.1% of the isobutane are oxidised to CO_2 and H_2O from a 6:4 mixture of the two compounds at 315°. On the same catalyst propylene and but-2-ene are oxidised fully and selectively in the presence of isobutane. Thus, these systems show the molecular sieve effect.

One of the earliest studies of the deep oxidation of hydrocarbons was on zeolites not containing transition metals[51]. The activities of NaX, CaX, and MnX zeolites towards the oxidation of hexane isomers were compared, and MnX (i.e. a zeolite containing cations of a typical transition metal) was found to be inferior to NaX zeolite in its activity towards deep oxidation. The catalysts were placed in the following series with respect to the extent of carbon formation: CaX > MnX > NaX. The authors[51] point out that the zeolite reaction does not correspond to the typical oxidation–reduction mechanism of transition metal oxides, since NaX is more active than MnX. Gradual replacement of the sodium by bivalent cations suppresses the oxidative activity, and the cracking reaction becomes predominant.

Recent scientific papers and patent applications highlight the high activity of zeolites towards the oxidation of various substances. Thus, Doronina and coworkers[52] studied the catalytic behaviour of the zeolites NaA, NaX, NaY, PdY, NiY, CoY, Pd-mordenite, and Tseokar-2 towards the deep oxidation of chlorinated organic compounds. At 400–450° over 90% oxidation was obtained on NaY, PdY, CoY, and Pd-mordenite. Selective oxidation of hexafluoropropylene takes place on catalysts consisting of NaY zeolite in which the Na atoms have been replaced by Cr, Mn, Fe, Ni, Pd, or Ce ions to an extent greater than 50 equiv.%.[53] A substantial level of activity towards this reaction was obtained also with samples prepared by steeping NaY zeolite and amorphous alumina–silica in an aqueous solution of copper nitrate[53,54]: the extent of conversion was 15.0 to 29.1% at 250–300°, with a selectivity of 45.1–47.7%. A high activity towards the deep oxidation of carbon compounds at relatively low temperatures (<150°) has been observed with synthetic zeolites steeped in a solution of $H_2PtCl_6 \cdot 6H_2O$ in an organic solvent[55] and with ZSM-5 zeolite containing copper cations[56]. The increasing number of publications on the deep oxidation of various compounds in the presence of zeolite catalysts shows the importance of this topic.

We may conclude from published results that low-molecular-weight hydrocarbons on the whole undergo deep oxidation on zeolites, those containing transition-metal cations usually being the most active. As the molecular weight of the hydrocarbon increases, oxidative dehydrogenation may occur in parallel with the deep oxidation, but this phenomenon has not been studied extensively so far. Thus, Al'tshuler and Tsitovskaya[57] suggested the following method of preparing catalysts for the oxidative dehydrogenation of paraffins in the presence of halogens: a sample of Na-mordenite zeolite is steeped in an aqueous solution of H_2PtCl_6, dried at 140°, baked in air at 380°, and reduced in hydrogen at the same temperature. The sodium cations are then exchanged by caesium cations. In the presence of this catalyst the conversion of n-butane is 37.1%, with a selectivity of 79.2% towards butylenes and divinyl, for a mixture of reactants in the molar ratio n-butane : O_2 : Br_2 = 1:2:0.7.

In a study of the oxidative dehydrogenation of isopentane on zeolite catalysts[58,59] the conversion of isopentane on CaA, CaX, and CaY at 540° and a molar ratio iso-C_5H_{12} : O_2 = 1:1.8 was found to increase with the pore size of the zeolite, but the selectivity of the process was low[58]. In the case of type A zeolite containing Fe(III), Cr(III), Co(III), or

Zn(II) cations a direct relationship is observed between the extent of conversion of isopentane and the ionic radius of cations with the same charge[59]. The selectivity of the reaction towards isopentylenes and isoprene is not greater than 26%.

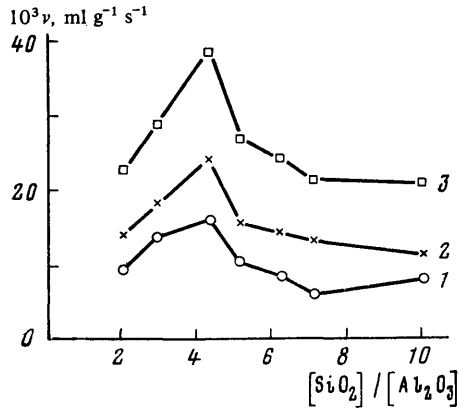


Figure 1. Rate of oxidative dehydrogenation of 2-methylbut-2-ene against the $[SiO_2]/[Al_2O_3]$ ratio in zeolite at: *1*) 400, *2*) 425, and *3*) 450 °C (Ref.60).

A study[60] of the effect of the composition and structure of the zeolites on the oxidative hydrogenation of 2-methylbut-2-ene showed that, in addition to oxidative dehydrogenation, zeolite catalysts can induce deep oxidation, isomerisation of the double bond, and cracking reactions. The yield of isoprene and the selectivity of the process are particularly sensitive to the zeolite structure. A comparison of the activities of the Na forms of A, X, and Y synthetic zeolites, chabazite, erionite L, and mordenite showed that the reaction rate goes through a maximum (corresponding to type Y zeolite) as the ratio of silicon to aluminium oxides is varied (see Fig.1). The apparent activation energy for Na-faujasite is ~15 kcal $mole^{-1}$, increasing to 18–20 kcal $mole^{-1}$ for type A zeolites, chabazite, erionite, and mordenite. The faujasites are superior to the narrow-pore zeolites in the yield of isoprene and in the selectivity of the process, but the latter are more active towards deep oxidation. In other words, X and Y zeolites behave differently from zeolites with narrow pores towards the oxidative dehydrogenation of 2-methylbut-2-ene.

The interaction of 2-methylbut-2-ene with different zeolites has been studied also by programmed thermo-desorption[61]. The thermo-desorption spectra of X, Y, and L zeolites were found to include three peaks (at 75–80, 130–170, and 200–300° respectively), though the adsorption capacity of faujasites for this compound is much greater than that of type L zeolites. With chabazite and erionite only one desorption peak is observed (t_{max} = 125–150°), and with type A zeolite two peaks with t_{max} at 150–160 and 300–350° respectively (Fig.2). This difference in the interaction of 2-methylbut-2-ene with different Na-zeolites accounts for the difference in activity and selectivity between faujasites and narrow-pore zeolites.

The effect of the nature of the exchangeable cation in type Y zeolite on the oxidative dehydrogenation of 2-methylbut-2-ene has also been studied[60]: as the ionic radius increases in the sequence Li < Na < K < Rb the yield of isoprene and the selectivity of the reaction decrease, and the yield of carbon oxides increases. At 400–450° a linear decrease of the reaction rate with increase of the ionic radius of the alkali metal cation is observed. It may be due to variations in the electrostatic field within the zeolite holes, or alternatively it may be due to the blocking effect of the larger cations on the "windows" leading to the large zeolite holes, which could hinder the diffusion of hydrocarbon molecules.

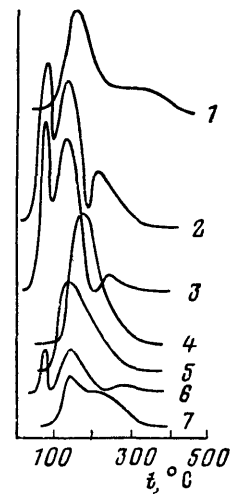


Figure 2. Thermo-desorption spectra of 2-methylbut-2-ene on zeolites: *1*) NaA, *2*) NaX, *3*) NaY, *4*) Na-chabazite, *5*) Na-erionite, *6*) NaL, *7*) Na-mordenite (Ref.61).

III. OXIDATIVE TRANSFORMATIONS OF NAPHTHENES

The oxidation of cyclohexane on zeolite catalysts has been studied in detail in the Soviet Union and in Japan. Using type Y zeolites containing copper cations the main products were found[62] to be benzene, CO_2, and H_2O. Cu(II)Y zeolite is more active than the conventional catalyst for this reaction (CuO on silica gel). For conversions up to 10% the selectivity of the reaction with respect to benzene can be as high as 80%. In addition to the Cu(II) form, type Y zeolites containing Pd(II), Ag(I), Zn(II), Ni(II), and Cr(III) were also investigated. Cu(II)Y was found to be the most active in the formation of benzene, and Pd(II)Y in the deep oxidation reaction. The authors point out[62] that the most active catalysts have the highest activation energies and frequency factors. The dependence of the initial rates of formation of benzene and of carbon dioxide on the standard heat of formation of the metal oxide is described by curves with two peaks[63]. Similar relationships are observed for the dehydrogenation of cyclohexane to benzene on oxide catalysts[64,65], but in this case the activity maximum corresponds to the catalyst Cr_2O_3.

NaY zeolite was found[66,67] to be active only towards the deep oxidation of cyclohexane (which sets in at temperatures as low as 150–160°). In contrast to the reaction on NaY, the oxidation of cyclohexane on the Cu(II) and Fe(III) forms of type Y zeolite begins at 240–260°, and proceeds

in two directions: deep oxidation, and oxidative dehydrogenation to benzene. As the degree of exchange of the sodium cations by transition metal cations is increased, the yield of benzene increases, but the specific activity of the catalyst [expressed for one Cu(II) or Fe(III) ion] decreases. The selectivity of the reaction towards benzene and the concentration of mobile oxygen in the zeolite increase with the exchange of sodium cations by transition metal cations. Mobile oxygen atoms are absent in Mn(II)Y, Co(III)Y, and Zn(II)Y zeolites: these materials behave like NaY zeolite, giving only deep oxidation products. On the other hand the zeolites containing Cu(II), Fe(III), Cr(III), and Ni(II) cations (active towards the oxidative dehydrogenation of cyclohexane) contain "active" oxygen. It has been pointed out[66,67] that the selectivity of the benzene formation reaction is higher in crystalline alumina–silicas containing transition metal ions than in the amorphous catalysts containing the same transition metals.

Spectral studies by the pulse method[68] have demonstrated the strong adsorption of cyclohexane on NaY zeolite in the pre-catalytic temperature region. After exposure to a $C_6H_{12} + O_2$ mixture, even at 60–80°, NaY zeolite shows characteristic absorption bands at 1720, 1780, and 1820 cm^{-2} (corresponding to carbonyl and peroxide compounds). After partial replacement of the sodium ions by Cu(II) these compounds are no longer observed (up to 180°).

An interesting feature of the deep oxidation of cyclohexane on NaX and NaY zeolites in the development of an oscillatory (autocatalytic) oxidation regime, ascribed[68,69] to periodic increases in the concentration of peroxide compounds on the zeolite surface. By studying the effect of temperature on this process it was shown that the oxidation of cyclohexane on Na faujasites has a mixed (homogeneous–heterogeneous) mechanism[68–70]. The penetration of the reaction into the gas phase occurs at 120° in the case of NaY, and at 220° in the case of zeolites containing transition metals. According to Elinek and coworkers[70] the relative extent of the homogeneous reaction exceeds 60% when the reaction mixture contains 0.3–0.6 vol.% of cyclohexane.

By applying thermo-desorption and calorimetry methods to the cyclohexane–NaX system it was shown[71] that cyclohexane is adsorbed in one form only, with an activation energy for desorption of 18 kcal $mole^{-1}$ in a stream of helium and 13 kcal $mole^{-1}$ in air. In both cases the adsorption is reversible, and almost the whole of the adsorbed cyclohexane is evolved during the desorption. This excludes any mechanism which explains the oscillatory regime (i.e. periodic changes in extent of conversion and in temperature) by postulating several forms of adsorbed cyclohexane. The heat of adsorption of the cyclohexane is independent of the surface coverage of the catalyst, showing that the surface is energetically uniform towards cyclohexane, and allowing the dependence of the activation energy of one of the steps on the coverage of the surface by the reactant to be rejected as an explanation of the oscillations occurring during the oxidation of cyclohexane. On the basis of these results the authors suggest[71] that when cyclohexane and oxygen are added sequentially peroxide compounds are formed by the reaction of cyclohexane with the free radical forms of adsorbed oxygen, further oxidation involving oxygen from the gas phase. The marked dependence of the reaction rate on the concentration of oxygen in the reaction mixture is interpreted[72] as evidence for the participation of oxygen in the chain propagation reactions.

The kinetics of the oxidative dehydrogenation of cyclohexane on Cu(II)Y zeolite were studied by Elinek and coworkers[73]. The rates of oxidative dehydrogenation and of deep oxidation of cyclohexane were found to depend on the partial pressures of the reactants according to the equations

$$v(\text{benzene}) = k \cdot p_{O_2}$$

$$v(CO_2) = k' \cdot p_{O_2}^{0.5} .$$

Thus the rates of both reactions are practically independent of the partial pressure of cyclohexane.

By studying the adsorption of oxygen and cyclohexane on the catalysts by the chromatographic pulse method, with the reactants introduced in different orders, the adsorption of oxygen was found to be rate-determining in the oxidative dehydrogenation of cyclohexane to give benzene. The high yields of benzene in the presence of Cu(II)Y are due to the high adsorption capacity of this zeolite towards oxygen. The rates of deep oxidation and of oxidative dehydrogenation of cyclohexane at 290° are given in Table 1, together with the adsorption capacities of various cationic forms of type Y zeolite towards cyclohexane and oxygen[73]. For low degrees of exchange of sodium by copper cations the reaction products contain only a small amount of cyclohexane (<1%), and on the samples with a high Cu(II) content no cyclohexane can be detected. According to these results the authors[73] propose the following scheme for the transformations of cyclohexane on zeolites:

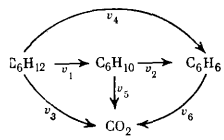


Table 1. Catalytic activity (α) and adsorption capacity (γ) of the cationic forms of type Y zeolite[73].

Catalysts	$10^2 \alpha$*, ml g^{-1} min^{-1}		γ**	
	$v(C_6H_6)$	$v(CO_2)$	C_6H_{12}	O_2
Cu (II) Y	52.0	22.0	100	100
Pd (II) Y	4.4	7250.0	200	<1***
Cr (III) Y	2.3	9.6	<1	<1
Zn (II) Y	0.4	3.2	<1	<1
Ni (II) Y	1.4	7.3	<1	<1
Ag (I) Y	0.2	2.5	<1	<1

*Rate of the reaction at 290°.

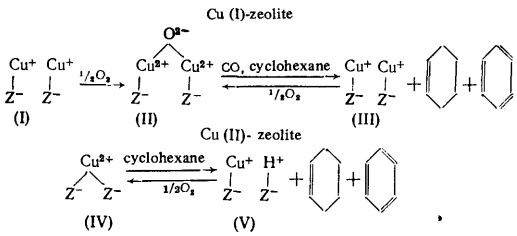
**The adsorption capacity of Cu(II)Y zeolite is arbitrarily taken as 100.

***On Pd(II)Y benzene is formed by dehydrogenation of cyclohexane without involving oxygen.

The oxidation of cyclohexane, ethylene, and CO on type Y zeolites containing Fe(III), Fe(II), Cu(II), and Cu(I) cations has been studied[74], and the Cu(I)Y and Fe(II)Y zeolites were found to be catalytically more active towards the oxidation of CO than Cu(II)Y and Fe(III)Y zeolites. This is explained in terms of the amount of oxygen chemisorbed on the catalyst [negligibly small in the case of catalysts containing Cu(II) and Fe(III) ions]. A further increase in the valency of these ions is energetically very difficult, whereas oxygen chemisorption on zeolites containing Cu(I) and Fe(II) can readily take place, to give a 0.44–0.5 ratio of the numbers of oxygen atoms and metal ions. The authors[74] point out that Cu(II) zeolite has a small but measurable

activity although oxygen adsorption on this material is undetectable, and they explain this observation by postulating activation of the oxygen in the zeolite structure by the added copper.

In contrast to the oxidation of CO, in the oxidative dehydrogenation of cyclohexane no difference was found between the catalytic activities of Cu(II)Y and Cu(I)Y [or Fe(III)Y and Fe(II)Y]. The behaviour of the system is explained[74] by postulating the following reaction schemes for Cu(I) and Cu(II) zeolites:



In these equations Z^- is the anionic form of the zeolite. In the oxidation of CO, which requires the presence of active O^{2-}, the preferred structure is (II). However, in the dehydrogenation of cyclohexane structures (II) and (IV) have equal activities. An analogous mechanism can be written for Fe(II) and Fe(III) zeolites.

The selectivity of the formation of benzene by the oxidative dehydrogenation of cyclohexane on Cu(I)Y, Cu(II)Y, Cu(II)-mordenite, and CuO/SiO_2 catalysts was found[75] to be 83, 76, 0.44, and 33% respectively, with activation energies of 27, 18, 38, and 20 kcal $mole^{-1}$. The kinetic order of the reaction with respect to oxygen was 1 on Cu(II)Y zeolite and 0.5 on Cu(I)Y. Cyclopentane on these catalysts undergoes mainly deep oxidation: whereas in the presence of Cu(I)Y the rate of oxidation of cyclohexane is almost an order of magnitude greater than that of cyclopentane, in the presence of Cu(II)Y the two rates are almost equal. Furthermore, the activity of Cu(I) towards the oxidation of cyclopentane rapidly decays with time, whereas the activity of Cu(II)Y is relatively stable. These differences between the catalytic properties of copper-containing zeolites are explained[75] by postulating the participation of O_2 in the oxidation on Cu(II)Y and of dissociatively adsorbed oxygen in the oxidation on Cu(I)Y.

The dehydrogenation of cyclohexane on various cationic forms of type X zeolite has been studied[76-78] both in the presence and in the absence of oxygen. Na-, Ca-, and decationated forms were found to be practically inactive towards the formation of benzene, but the introduction of nickel cations creates dehydrogenation activity which increases with the amount of nickel added to the sample. In the presence of oxygen the Ni-containing zeolites are active also in the oxidative dehydrogenation with formation of benzene, whereas the activity of NaX is high only towards deep oxidation. As the amount of sodium in the zeolite decreases the extent of the deep oxidation reaction also decreases very markedly. The most active and selective catalyst for the formation of benzene is a sample in which 25% of the sodium has been exchanged by nickel cations and 33% by hydrogen ions.

An interesting feature of the Fe(II) form of type Y zeolite has been pointed out[79]: the production of cyclohexene by the oxidative degradation of cyclohexane. In a pulsed regime at 180° the conversion of cyclohexane is 2.5%, with 58% selectivity for cyclohexene. The Co(II)Y, Cu(II)Y, and Cr(III)Y zeolites show a lower activity and selectivity for the formation of cyclohexene. Increasing the partial pressure of oxygen in the reaction mixture and the contact time increases the conversion, but it lowers the selectivity for cyclohexene. On Fe(II)X zeolite, and in the presence of water vapour, the conversion of cyclohexane at 260° is 14%, and the selectivity for cyclohexene is 30%.[80] The Fe-mordenite catalyst shows no activity towards the formation of cyclohexene up to 430°. Thus, the activity of iron-containing zeolites towards the formation of cyclohexene decreases in the sequence FeX > FeY > Fe-mordenite. Kubo and coworkers[80] suggested, in the light of published results[81-83], that dissociatively adsorbed oxygen [detected by γ-resonance spectroscopy on Fe(II) zeolites] plays an important role in this reaction on low-valency cationic forms of faujasite.

Later work on the oxidation of cyclohexane on crystalline aluminosilicates showed that the direction of the reaction is also strongly influenced by the structure of the zeolite. Thus, whereas faujasites catalyse the reaction (depending on the nature of the exchanged cation) towards deep oxidation of the cyclohexane or towards oxidative dehydrogenation with formation of benzene, in the case of the alkali metal forms of synthetic type A zeolites and of sodalite, chabazite, erionite, and mordenite the oxidative dehydrogenation of cyclohexane stops at the cyclohexene stage[84-91]. On the more active catalysts the yield of cyclohexene is greater than 20%, which is almost 5–10 times greater than the activity of Fe(II)-containing faujasites. Table 2 shows some results on the activity and selectivity of zeolite catalysts towards the oxidative dehydrogenation of cyclohexane to cyclohexene[85-88]. The tabulated values show that the introduction of transition metal cations (Pd, Cu, Fe) into the zeolite composition lowers the selectivity for this reaction (in comparison to the alkali metal cation forms). Thus, in contrast to the Na faujasites (which are active only towards deep oxidation), the Na forms of narrow-pore zeolites cannot accommodate the cyclohexane molecules in the internal zeolite holes, and on these catalysts the oxidative dehydrogenation stops at the stage of cyclohexene formation.

Table 2. Oxidative dehydrogenation of cyclohexane on zeolites (molar ratio $C_6H_{12}:O_2 = 1:1.5$; $V = 1\ h^{-1}$)*.[88]

Zeolite	$[SiO_2]/[Al_2O_3]$	t, °C	Conversion, %	$W_{C_6H_{10}}$, %	S, %
NaA	2.0	400	25.6	18.3	71
Na-sodalite	2.0	400	23.1	16.0	69
Na, K-chabazite	5.1	450	28.3	20.5	73
0.08Pd-chabazite	5.1	450	26.1	18.3	70
Na, K-erionite	6.2	450	25.3	19.2	76
0.08Pd-erionite	6.2	450	33.6	20.9	62
0.25Fe-erionite	6.2	450	28.5	18.3	64
0.30Cu-erionite	6.2	450	20.0	13.5	67
Na, K-L	7.1	400	15.2	12.3	81
Na-mordenite	10.0	400	16.3	13.4	82
0.08Pd-mordenite	10.0	400	17.2	14.4	78
Clinoptilolite**	~10	400	20.2	16.1	80

*Symbols: V is the volume velocity for cyclohexane, $W_{C_6H_{10}}$ is the yield of cyclohexene, S is the selectivity of the reaction.

**Molar ratio $C_6H_{12}:O_2 = 1:1$, $V = 0.5\ h^{-1}$.

A study of the interaction of cyclohexane with various zeolites by the thermo-desorption method[89] has shown that cyclohexane is adsorbed only on type X and Y zeolites, and to a smaller extent on type L zeolite. Hence it was suggested that the strong adsorption on faujasites is responsible for the deep oxidation of cyclohexane on zeolites.

But although L type zeolite adsorbs cyclohexane, its adsorption capacity is very low. This may be the reason for the low yield of cyclohexene (as compared with other narrow-pore zeolites) of this catalyst, which occupies a position intermediate between the narrow-pore catalysts and the faujasites.

The t_{max} value of the cyclohexane desorption peak on different cationic forms of zeolite Y is displaced towards lower temperatures as the initial NaY zeolite is converted into the working form: in other words, the strength of the adsorbate–adsorbent bond is lowered, and the effective diffusion coefficient increases almost by two orders of magnitude[89]. These changes affect the catalytic properties of the samples. Unlike NaY, which catalyses only the deep oxidation of cyclohexane, NdY catalyses the oxidative dehydrogenation of this compound to give benzene. On the other hand, with narrow-pore zeolites (which do not, in general, adsorb cyclohexane) the main product is cyclohexene.

The kinetics of the oxidative dehydrogenation of cyclohexane in the presence of Na, K-erionite have been studied in our laboratory[88]. The reaction is first-order in oxygen, and has a fractional order with respect to cyclohexane. The apparent activation energy is only 5.5 kcal mole^{-1}. The rate-limiting step is assumed to be the surface reaction between cyclohexane and the weakly adsorbed molecular oxygen. The experimental results are satisfactorily described by the equation

$$v = \frac{k \cdot p_{O_2} p_{C_6H_{12}}}{1 + a_{C_6H_{12}} p_{C_6H_{12}}},$$

where $a_{C_6H_{12}}$ is the adsorption coefficient of cyclohexane.

Table 3. Oxidative dehydrogenation of cyclohexene on zeolites (450 °C, $C_6H_{10}:O_2 = 1:1$, $V = 1\ h^{-1}$).[88]

Zeolite	Conversion, %	W, %		S, %	
		C_6H_8	C_6H_6	C_6H_8	C_6H_6
Na	7.3	2.9	3.9	38	53
Na, K-chabazite	16.1	7.7	7.7	48	48
0.08Pd-chabazite	9.1	3.3	5.4	36	59
Na, K-erionite	8.3	3.4	3.4	41	41
0.08Pd-erionite	10.2	1.4	7.2	14	71
0.25Fe-erionite	11.9	1.3	7.1	11	60
0.30Cu-erionite	11.4	0.8	6.2	7	54
Na, K-L	6.7	2.4	3.3	36	49
Na-mordenite	10.4	3.3	4.2	32	40
0.08Pd-mordenite	10.0	2.3	5.5	23	50

Since the oxidative dehydrogenation of cyclohexane on narrow-pore zeolites stops at the cyclohexene formation stage, we examined[88] the possibility of preparing cyclohexadiene by the oxidative dehydrogenation of cyclohexene. The results (Table 3) show that (except in the case of Na, K-chabazite sample) the yield of cyclohexadiene is 3.4% or less, and the selectivity of the reaction varies between 7 and 48%. An increase in temperature or in the oxygen to cyclohexene concentration ratio favours the yield of benzene and thus lowers the selectivity for cyclohexadiene. The introduction of transition-metal cations into the zeolite also results in a lower selectivity.

We have also studied[90] the oxidative dehydrogenation of cyclohexane on natural zeolites (thomsonite, stilbite, natrolite, analcite, lomontite, mordenite, heulandite, and clinoptilolite). On all these samples the reaction was found to yield mainly cyclohexene: the highest activity was observed with a zeolite sample of the thomsonite type, which gave a 20.8% yield of cyclohexene at 450° with a selectivity of 80%. The zeolite structure has a marked effect on the temperature dependence of the yield of cyclohexene (Fig.3). In some cases the yield goes through a maximum at 400° (clinoptilolite and heulandite), whereas with thomsonite the yield continues to increase with temperature up to 450°. However, at still higher temperatures the selectivity decreases in every case.

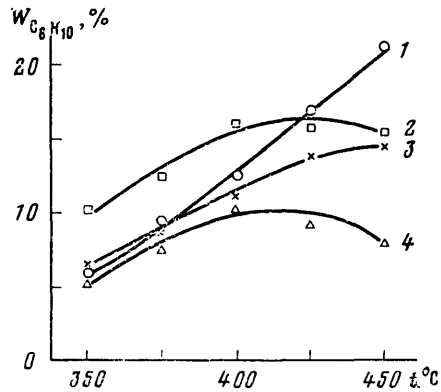


Figure 3. Yield of cyclohexene against temperature for natural zeolite types: *1*) thomsonite, *2*) clinoptilolite, *3*) stilbite, *4*) heulandite[90].

Table 4. Oxidative dehydrogenation of methylcyclohexane on zeolites (450°, $CH_3C_6H_{11}:O_2 = 1:1.3$, volume velocity for methylcyclohexane $1\ h^{-1}$).[97]

Zeolite	Composition of product, %				W_{CO_2}, %
	C_6H_{12}	$CH_3C_6H_{11}$	$CH_3C_6H_8$	$CH_3C_6H_5$	
NaA	1.2	61.3	12.2	24.5	4.2
NaX	0.5	60.0	3.5	35.5	6.9
NaY	0.4	63.0	3.1	33.0	6.6
Na, K-chabazite	1.0	67.9	12.4	15.8	3.1
Na, K-erionite	0.3	77.4	13.6	8.4	2.8
0.25Fe-erionite	0.2	63.1	10.3	25.6	7.0
0.35Cu-erionite	1.3	60.5	11.2	26.2	5.1
Na, K-L	0.5	61.0	9.7	27.8	3.6
Na-mordenite	0.5	62.1	8.3	28.7	4.0

The influence of the structure and composition of the zeolite on the course of the reaction is even more marked in the oxidation of methylcyclohexane. The main product of the dehydrogenation of methylcyclohexane on metallic or oxide catalysts is toluene. There are published reports that only toluene is formed by the dehydrogenation of methylcyclohexane on 0.5% PtNaY zeolite[92], and that the partial dehydrogenation products which are formed in small quantities are converted into carbon. By studying the kinetics of the reaction and the carbonisation of the catalyst the authors concluded[92] that an intermediate dehydrogenation step is involved.

A recent patent[93] discloses that the reaction of methylcyclohexane on PtCaY zeolite at 505° yields toluent (55.2%), benzene (12.3%), and xylenes (17.0%). The bifunctional PtCaY catalyst apparently catalyses the dehydrogenation (on the platinum) of methylcyclohexane to toluene, which then undergoes disproportionation of the methyl group (on the acidic centres) to give benzene and xylenes. The dehydrogenation of alkylcyclanes to the corresponding aromatic hydrocarbons in the presence of Pt-zeolite catalysts has also been reported[94].

The oxidative dehydrogenation of methylcyclohexane on zeolite catalysts is discussed in detail in Refs.91 and 95–97, and it is shown that the direction of the reaction, the yields of the various products, and the selectivities of the process are a function of the composition and structure of the zeolite. Thus, on Na-faujasite the main reactions of methylcyclohexane are deep oxidation and oxidative dehydrogenation with formation of toluene[95]. The alkali cationic forms of chabazite and erionite are more active and selective towards the formation of methylcyclohexenes[97], but the type A and L zeolites (and mordenite) have a lower selectivity towards methylcyclohexenes than chabazite and erionite, though they yield methylcyclohexenes as well as toluene (Table 4). The low selectivity of the faujasites with respect to methylcyclohexenes can be explained, as in the cyclohexane reaction, by the strong adsorption of methylcyclohexane on these zeolites, which favours the more disruptive transformations within the internal cavities on the zeolite. On the other hand, on the narrow-pore zeolites the reaction takes place on the outer crystal surfaces, and the resulting cyclo-olefin intermediates can be desorbed into the gas phase and escape further dehydrogenation to toluene.

Table 5. Conversion of methylcyclohexane on cationic forms of type Y zeolite (450°, volume velocity 1 h^{-1}).[96]

Zeolite	Carrier gas	Conversion, %	Composition of product, %					W_{CO_2}, %
			C_6H_6	$CH_3C_6H_5$	$C_2H_5C_6H_5$	$(CH_3)_2C_6H_4$	$(CH_3)_3C_6H_3$	
0.48 HY	air	85.4	3.2	38.7	—	22.3	—	4.0
0.48 HY	helium	64.4	—	16.1	—	9.1	—	—
0.86 CaY	air	96.2	2.0	43.2	0.9	35.6	3.5	3.7
0.86 CaY	helium	48.0	1.3	8.7	0.2	8.3	1.6	—
0.60 MgY	air	85.9	1.5	31.5	—	9.2	—	3.6
0.60 MgY	helium	48.4	—	8.5	—	1.4	—	—
0.93 NdY	air	95.5	2.9	45.9	0.9	34.8	—	3.3
0.93 NdY	helium	90.8	1.3	38.5	1.0	28.4	—	—
0.60 NiY*	air	64.5	2.0	12.9	0.9	20.9	4.1	3.8
0.60 NiY*	helium	58.8	1.1	22.0	0.5	17.2	2.3	—
0.50 CoY	air	31.1	1.4	8.2	—	—	—	4.9
0.50 CoY	helium	10.3	—	2.5	—	—	—	—

*At 350 °C.

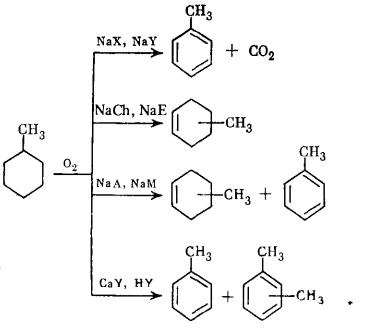
We note from Table 4 that the insertion of copper and iron cations into erionite increases the yields of toluene and carbon dioxide and thus lowers the selectivity of the reaction towards methylcyclohexenes[95]: in other words, zeolites containing transition metal cations tend to favour the more radical transformations of methylcyclohexane.

It has been shown[91,96] that in the presence of oxygen methylcyclohexane (unlike cyclohexane) reacts on decationated and on alkaline-earth cationic forms of type Y zeolite to give various aromatic hydrocarbons including toluene and xylenes (Table 5). In other words, the Ca, Mg, and NH_4 forms of type Y zeolite behave as typical bifunctional catalysts towards the oxidative transformation of methylcyclohexane into xylenes, even though their composition does not include Group VIII metals or transition-metal oxides. We may assume that the xylenes are formed by the oxidative dehydrogenation of methylcyclohexane to toluene, followed by disproportionation into benzene and xylenes. However, it appears from the distribution of products that benzene is always present in smaller amounts than the xylenes. Furthermore, under otherwise identical conditions the yield of xylenes from the disproportionation of toluene is smaller than from the reaction of methylcyclohexane, and therefore an alternative mechanism for the formation of xylenes from methylcyclohexane (by-passing the toluene formation step) cannot be excluded.

In a study[96] of the effect of the degree of decationation of type Y zeolite on the reaction of methylcyclohexane it was found that the yield of xylenes becomes progressively less sensitive to the presence of oxygen in the reaction mixture as the degree of decationation of the zeolite is increased. It has also been reported[98] that on decationated zeolite Y containing 3% Rh methylcyclohexane at 300° and 30 atm pressure undergoes isomerisation and hydrogenolysis reactions, giving various five-membered cyclic and aliphatic hydrocarbons.

The lack of activity of the alkali cationic forms of various zeolites and of amorphous alumina–silicas and aluminium oxide towards the oxidative conversion of methylcyclohexane into xylenes suggests that both acidic properties and a specific crystal structure are required to give an active catalyst[96]. Thus, decationated mordenite has a negligibly small activity for this reaction, and CaX zeolite gives a much smaller yield of xylenes than CaY.

The following reaction scheme reflects the main directions of the oxidative dehydrogenation of methylcyclohexane on zeolite catalysts (NaCh, NaE, and NaM are Na-chabazite, Na-erionite, and Na-mordenite respectively):



By varying the structure and composition of the zeolites over a wide range we can control the direction of the transformation of methylcyclohexane, and thus obtain desirable end-products. This flexible and selective application suggests that crystalline alumina–silicas will be used increasingly as practical oxidation catalysts.

IV. OXIDATIVE DEHYDROGENATION OF ALKYLAROMATIC HYDROCARBONS

The oxidative dehydrogenation of ethylbenzene on type Y zeolite containing transition metals was first reported by Venuto and Landies[5]. On MnY zeolite the yield of styrene was not higher than 8.7%. This low activity did not justify a detailed study of the oxidative dehydrogenation of alkylaromatic hydrocarbons on other types of zeolite.

However, more recent work[85,87,99-111] has revealed a number of interesting aspects of this reaction in the presence of zeolite catalysts. Thus, unlike the MnY zeolite, alkali cationic forms of various zeolites (free from transition metals) are catalytically active in the oxidative dehydrogenation of ethylbenzene and isopropylbenzene[87,95,100], the activity and selectivity of the catalysts and the specific features of the process being strongly influenced by the zeolite structure. Faujasites were found[100,104] to be more active towards deep oxidation, and therefore their selectivity towards oxidation dehydrogenation is low. Narrow-pore type A zeolites, chabazite, erionite, and mordenite are less active towards the deep oxidation and hence they offer a higher selectivity for the formation of styrene. Furthermore the yield of styrene on faujasites increases with time, a stable regime being established 2.5–3 h after the beginning of the reaction, whereas in the presence of narrow-pore zeolites this development period is not observed.

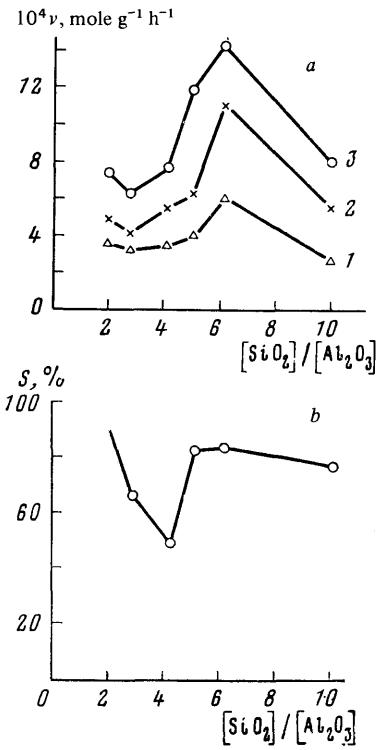


Figure 4. Rate of oxidative dehydrogenation of ethylbenzene (*a*) and selectivity with respect to styrene (*b*) against the $[SiO_2]/[Al_2O_3]$ ratio in zeolite at: *1*) 400, *2*) 425, and *3*) 450 °C (Ref.100).

The effect of the zeolite structure on the activity was investigated on the Na or Na, K forms of various synthetic zeolites[100]. The rates of oxidative dehydrogenation of ethylbenzene and the selectivities with respect to styrene are shown in Fig.4 as a function of the silica to alumina ratio in the zeolite[100]. In oxidation reactions with an O_2:ethylbenzene ratio of 0.4 the narrow-pore zeolites of the erionite type offer a higher activity and selectivity than the faujasites. It is interesting to note that on type A zeolites, chabazite, erionite, and mordenite, whose pores are too small to allow the ethylbenzene molecules to penetrate into the zeolite holes, the oxidative dehydrogenation takes place with a greater selectivity than on the wide-pore faujasites (Fig.4*b*).

Interesting results were obtained also in a study of the oxidative dehydrogenation of alkylaromatic hydrocarbons on synthetic sodalite[87], characterised by the smallest entry windows of any type of zeolite (2.6 Å), a high thermal stability, and a close-packed crystal lattice[17]. In the presence of Na-sodalite the reaction is detectable even at 350°, and at 525° the yield of styrene reaches 45%, making sodalite more active than any other synthetic zeolite towards the oxidative dehydrogenation of ethylbenzene.

The kinetics of the oxidative dehydrogenation of ethylbenzene on the Na, K form of erionite have been studied[102], and the reaction at 400–475° was found to be first-order in ethylbenzene. At temperatures below 425° a zero reaction order with respect to oxygen is observed, and at higher temperatures the dependence is of the Langmuir type. The rate-limiting step of the reaction is thought to be the interaction between weakly adsorbed ethylbenzene and oxygen on the outer surface of the zeolite crystals. The apparent activation energy is 31.5 kcal $mole^{-1}$.

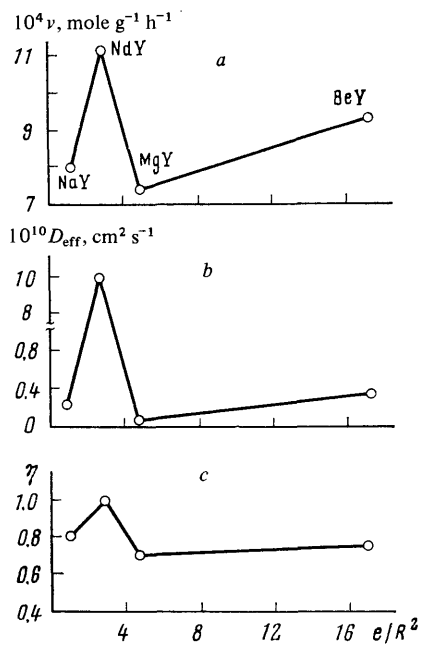


Figure 5. Rate of oxidative dehydrogenation of ethylbenzene (*a*), effective diffusion coefficient (*b*), and effectiveness factor (*c*) against the electrostatic potential of the cation in type Y zeolite at 425 °C (Ref.106).

The interaction of ethylbenzene with various zeolites has been studied by thermo-desorption[106]. Adsorption of ethylbenzene occurs only on type X and Y zeolites; only one desorption peak is observed, whatever the nature and concentration of the cation, and this peak is shifted towards lower temperatures when the sodium is exchanged for multivalent cations. Evidently, the strong adsorption of ethylbenzene on Na-faujasites is responsible for the deep oxidation

observed on these catalysts, and hence for the low selectivity with respect to styrene. From the thermo-desorption results we calculated[106] the activation energies for diffusion, the pre-exponential factors, and the effective diffusion coefficients of ethylbenzene in the zeolites. Plots of the rate of oxidative dehydrogenation of ethylbenzene, of the effective diffusion coefficient, and of the effectiveness factor against the electrostatic potential (e/R^2) of the cation in the zeolite are shown in Fig.5. We note that all three plots go through a maximum for the NdY zeolite, in which the reaction rate is least affected by diffusional limitations.

We have also studied[103,109] the catalytic properties of various types of natural zeolite towards the oxidative dehydrogenation of ethylbenzene and isopropylbenzene. The most active catalysts are heulandite and clinoptilolite, on which the yield of styrene varies between 37.7 and 48.2%. The apparent activation energy of the reaction for these natural zeolites is in the range 5–17 kcal mole^{-1}, i.e. it is lower than the apparent activation energy for synthetic zeolites of the chabazite, erionite, and mordenite types[100]. In the oxidative dehydrogenation of isopropylbenzene the catalysts form the same activity sequence as in the ethylbenzene reaction: the most active is clinoptilolite, and the least active lomontite. However, on all the zeolites the conversion of isopropylbenzene into α-methylstyrene is smaller than the conversion of ethylbenzene into styrene.

The catalytic properties of Pd-containing type Y zeolites towards the oxidative dehydrogenation of alkylaromatic hydrocarbons are discussed in Refs.101 and 107. It is shown that, unlike the starting NaY zeolite (which has a significant and stable activity towards the deep oxidation reaction), samples containing Pd(II) ions yield an amount of CO_2 which decreases as the time of operation of the catalyst increases, so that when steady state is reached the activity and selectivity of PdNaY towards styrene are relatively high. The activity and selectivity of this catalyst towards the oxidative dehydrogenation of ethylbenzene and isopropylbenzene are also higher than those of a Pd catalyst on amorphous alumina–silica.

The effect of the structure and composition of the zeolite on the activity of Pd-containing catalysts is discussed in Ref.110. Alkaline-earth and decationated forms of type Y zeolite have an initially high activity towards the cracking of ethylbenzene, but the yield of cracking products decreases with time, and after a development period small amounts of styrene can be detected. On an amorphous alumina–silica catalyst the yield of styrene decreases during the reaction. The introduction of palladium into CaY and HY zeolites and into amorphous alumina–silica lowers their cracking activity and increases the yield of deep oxidation and oxidative dehydrogenation products. However, all three samples are inferior to PdNaY zeolite in the yield of styrene and in the selectivity of the process. A possible explanation is electron deficiency of the palladium in CaY, HY, and amorphous alumina–silica as a result of the repulsion of the Pd 4*d* electrons by the acidic centres of the matrix. At the same time, because of the low acidity and of the weak electrostatic fields of the sodium cations, the influence of NaY on the valency state of the metal is much slighter[112]. We have shown[110] that the addition of Pd(II) cations to zeolites of the chabazite, erionite, and mordenite types increases their activity only in respect of deep oxidation, and as a result the Pd-containing zeolites of these types have a lower selectivity towards styrene formation than the initial zeolites.

The kinetics of the oxidative dehydrogenation of ethylbenzene on 0.5 wt.% PdNaY zeolite prepared by ion exchange have been investigated[111]. The reaction is kinetically of the first order with respect to ethylbenzene and of order 0.5 with respect to oxygen. The activation energy is 15 kcal mole^{-1}, i.e. about one-half of the activation energy of the same reaction on Na, K-erionite.[101]

By postulating the reaction scheme

$$O_2 + 2[\ ] \overset{k_1}{\rightleftarrows} 2[O]$$
$$C_2H_5C_6H_5 + [\ ] \overset{k_2}{\rightleftarrows} [C_2H_5C_6H_5]$$
$$[C_2H_5C_6H_5] + [O] \overset{k_3}{\rightleftarrows} [C_2H_3C_6H_5] + [H_2O]$$
$$[C_2H_3C_6H_5] \overset{k_4}{\rightleftarrows} C_2H_3C_6H_5 + [\ ]$$
$$[H_2O] \overset{k_5}{\rightleftarrows} H_2O + [\ ]$$

(where [ ] denotes an active centre on the catalyst surface, and [O], $[C_2H_5C_6H_5]$, $[C_2H_3C_6H_5]$, and $[H_2O]$ are adsorbed forms of oxygen, ethylbenzene, styrene, and water), and by taking as the slow step the desorption of styrene from the internal zeolite holes, we obtain the kinetic equation

$$v = v_{stat}(1 - e^{-k_4\tau})$$

where τ is time. This equation describes the changes in reaction rate in both the non-stationary and the stationary ($e^{-k_4\tau} \ll 1$) regime.

The oxidative dehydrogenation of ethylbenzene on the zeolite-containing catalysts AShNTs-3 and TsEOKAR-2 has been studied[113]. The yield of styrene at 525° on AShNTs-3 containing 20 wt.% of decationated zeolite Y was 31%; the selectivity of the process was 77%. The authors suggest[113] that the ethylbenzene molecule is adsorbed through the π-electrons of the benzene ring on a coordinationally unsaturated Al atom. On the "stronger" acidic centres the adsorption of ethylbenzene is stronger, and the molecule can undergo deep oxidation.

In the absence of oxygen isopropylbenzene can be dehydrogenated on zeolites[114,115] at high temperatures, but the selectivity is low and the reaction is accompanied by cracking of the initial hydrocarbon. Hence we may assume that the role of oxygen in oxidative dehydrogenation on zeolites is not to oxidise the hydrogen produced by the dehydrogenation of the hydrocarbon but to form carbon-containing intermediates which decompose to give styrene. This hypothesis is consistent with the low activity of zeolites containing no transition metals towards the dehydrogenation of hydrocarbons[114–117] and the oxidation of hydrogen[27,28].

V. OXIDATION OF INORGANIC COMPOUNDS

The reaction between hydrogen and oxygen is the simplest model reaction used to study the oxidation properties of catalysts. Ref.27 and 28 describe a study of the relative activities of type Y zeolites containing upwards of 50 equiv.% of transition-metal cations (Cu, Cr, Fe, Co, Mn, Ni, Ag). The highest activity was observed in AgY, followed by CuY, FeY, CrY, NiY, and CoY. The same activity sequence applies, on the whole, to the oxidation of CO, but in this reaction CoY is as active as AgY.

The activity of different cationic forms of type X zeolite towards the oxidation of hydrogen was found[118] to decrease in the series PdHX > CuHX > FeHX > NiHX > CrHX > ZnHX > MnHX > CoHX > HX. The activity of the CuHX sample increases with the concentration of copper ions in the zeolite. Copper cation pairs connected by bridging oxygen are suggested[118] as the active centres.

The main features of the oxidation of CO on zeolites containing transition metals are discussed in detail in Refs.119–127. The addition of up to 36% of copper is shown[119] to increase the activity in direct proportion, changing to an exponential dependence for copper contents

up to 90%. The reaction is first-order with respect to carbon monoxide and zero-order with respect to oxygen. The active centres are thought to contain more than one copper cation. The effect of the ion exchange conditions on the activity of the Cu(II), Cr(III), Ni(II), Co(III), and Fe(III) forms of type Y zeolite towards the oxidation of CO is discussed in Refs.120–122. Samples prepared at pH values corresponding to hydrolysis of the salts have a catalytic activity per atom 4–5 orders of magnitude greater than samples prepared under conditions in which the transition metals are stabilised as isolated ions. In the former case the metal cations are partly coordinated by an oxygen atom not belonging to the zeolite skeleton and having a high reactivity as a result of the greater covalence of its bond with the metal cation.

Isolated Cu(II) cations in zeolites have been shown[123] not to interact with CO at temperatures between −196 and 500°. Weak magnetic groups of associated Cu(II) cations form adsorption complexes with CO at temperatures between −196 and 100°, and at 300–500° they oxidise CO to CO_2 [the Cu(II) being reduced to Cu(I)]. Strong magnetic associations of Cu(II) cations, including bridging (non-skeleton) oxygen, can oxidise CO to CO_2 even at low temperatures.

A study of the oxidation of CO on X and Y zeolites containing cations with low charges has led to the conclusion[124] that CO molecules from the gas phase can react with dissociatively adsorbed oxygen in bridging positions. Very little oxygen is adsorbed on the Tl(I), Co(II), and Mn(II) forms, and none on the Cu(II) and Ni(II) forms, because of the difficulty of raising the oxidation state of these cations. The catalytic activity of all these samples is low. Zeolites containing Fe(II) and Cu(I) are more active, and they can chemisorb up to 0.5 oxygen atom per metal atom. The following reaction mechanism was proposed[124] from the kinetic results:

$$2\mathrm{Fe(II)} + {}^1/_2\mathrm{O_2} \rightarrow \mathrm{Fe(III)}{-}\mathrm{O^{2-}}{-}\mathrm{Fe(III)}$$
$$\mathrm{Fe(III)}{-}\mathrm{O^{2-}}{-}\mathrm{Fe(III)} + \mathrm{CO} \rightarrow 2\mathrm{Fe(II)} + \mathrm{CO_2}\,.$$

The series of decreasing activity for the oxidation of CO is given[125] as CoY > CuY > FeY > NaY > MnY. The activity of the initial NaY zeolite is quite high at 400° but falls off rapidly at lower temperatures. The authors conclude that the catalytic activity of these zeolites is determined by the presence of isolated metal cations on the surface. I.r. spectral studies have shown[126] that the interaction of CO and O_2 on the surface of zeolites containing transition-metal cations leads (at high temperatures) to the formation of physisorbed CO_2 and of surface carbonates, produced by the interaction of CO and O_2 with the cations.

A very steep, non-linear increase in the adsorption of CO on zeolite Y as a function of the degree of exchange of sodium by multivalent cations has been noted[127], and ascribed to the fact that the cations are located in S_1 sites where CO adsorption cannot take place.

Amorphisation of FeY and CoY by a shock wave[128] has little effect on the oxidation of CO. The activation energy changes by 1–2 kcal mole^{-1}, and the catalytic activity per atom remains almost the same. Obviously, the catalytic properties are determined mainly by the nature of the transition-metal ions in the zeolite and by the way in which these ions are bound to the surface.

A method of preparing a zeolite catalyst containing 10% of rare-earth elements and 0.3% of Pt for the re-oxidation of CO to CO_2 in the regeneration of cracking catalysts has been proposed[129]. The conversion of CO can be as high as 95.8%, and the catalyst is stable towards carbon, hydrogen, and olefins.

The oxidation of ammonia on Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Cr(III), and Ag(I) forms of type Y zeolite has been studied by a pulse method[27,28]. The reaction product on all the catalysts is molecular nitrogen, but on the Cr(III) and Ag(I) forms nitrous oxide is also found, the selectivity for this compound being ~25% on Ag(I)Y at 400°. A series–parallel reaction is postulated, in which the N_2O reacts with NH_3 to give N_2. The catalysts can be arranged in the following series of decreasing activity: CuY > CrY > AgY > CoY > FeY > NiY, MnY. We note that this activity sequence differs quite markedly from that of the corresponding oxide catalysts[130,131]: this may be due to differences in the type of chemical interaction during catalysis on zeolites and on oxides.

The oxidation of ammonia on Cu(II)Y zeolite at 160–185° was found to be kinetically of the first order in ammonia and of zero order in oxygen[132]. The activation energy is 36.7 ± 2.6 kcal mole^{-1} for samples with different extents of ion exchange. The presence of $[Cu(II)(NH_3)_4]^{2+}$ complexes in the large zeolite holes has been detected by ESR and i.r. spectroscopy. The authors suggest[132] rate limitation by the reduction of Cu(II) to Cu(I).

VI. OXIDATION OF OXYGEN- AND SULPHUR-CONTAINING COMPOUNDS

The conversion of methanol on zeolites in the presence of oxygen has been investigated[133–140]. On zeolites not containing transition metals the methanol was found to react only by an acid–base mechanism to give dehydration and etherification products[133,134]. In the presence of zeolites containing groups of associated cations the methanol is oxidised to CO, CO_2, and formaldehyde[134], and when the reaction is carried out on zeolites containing isolated transition metal cations the main product is ether.

On NaX zeolite containing 21.2% of Ag the conversion of methanol at 320–350° is 91%, with a selectivity of 87% towards formaldehyde[135]. In the presence of a large excess of oxygen the methanol is oxidised to CO_2 and H_2O almost quantitatively.

The effect of the preparative conditions on the activity of the Cu and Ag forms of types A and Y zeolites towards the oxidation of methanol is discussed in Ref.136. Conversion of the copper ions in the zeolite into an oxide ($\xrightarrow{H_2}$ Cu° $\xrightarrow{O_2}$ CuO) does not affect the yield of formaldehyde, but the overall extent of reaction increases because of an increase in the yield of CO and CO_2, which the authors ascribe[136] to the greater covalency of the Cu–O bond in CuO as compared to the Cu–O–Cu associated groups in zeolite. Reduction of the silver to the metallic state in zeolites increases the yield of formaldehyde very substantially, possibly by facilitating the electronic transitions attending the oxidative dehydrogenation of methanol.

Natural zeolites of the mordenite and clinoptilolite type have been used as methanol oxidation catalysts[137,138]. Decationation of mordenite lowers the yield of formaldehyde, while the yield of ether increases by a factor of 2. On the Cu form of mordenite the reaction sets in at a temperature 100 K lower than on the sodium or the decationated form[137]. Among the many cationic forms of clinoptilolite the highest activity and selectivity are found in the magnesium-containing decationated form[138].

On the Na, Ni, and Co forms of type X zeolite at temperatures below 300° the main product of the oxidation of methanol is dimethyl ether, but when the temperature is raised to 450° a large proportion of the ether is converted

into formaldehyde[139]. The specific catalytic activity of the samples goes through a maximum as the degree of exchange is increased, and decreases in the sequence NiX > CoX > NaX. The authors[139] point out that the activity of CoX samples with a low degree of exchange is not very different from that of the NaX zeolite. They suggest that the reaction involves either oxygen in the coordination sphere of the cation (non-skeleton oxygen) or oxygen resulting from the dissociative adsorption of O_2 from the gas phase on the zeolite.

CH_3OH, CH_4, and NO are oxidised on NaX zeolite after u.v. irradiation[140], with formation of surface carbonate, formate, and nitrate complexes. As in the case of some metal oxides, these photo-stimulated reactions on NaX zeolite seem to be associated with the presence of impurities or structural defects. According to Shchuklov and coworkers[141] the impurity centres consisting of a transition metal ion in zeolites can capture an electron and thus stabilise the chemically active positive holes formed by the u.v. irradiation. Stabilisation of the free radicals formed by the decomposition of organic peroxides can occur by an electron-donor or an electron-acceptor mechanism on the surface of NaX and NaY zeolites[142].

In an oxidising medium, isopropanol reacts on the polycationic Fe–Zn form of type A zeolite to give acetone[143]. The activity of the Fe–Zn form is much greater than that of the separate Fe and Zn forms of type A zeolite. The yield of acetone increases with the degree of exchange, but the order in which the Fe and Zn ions are introduced into the zeolite has little effect on the activity. It has been shown[144] that, unlike the Li and Na forms of type X zeolite (which catalyse only the dehydration of isopropanol), the K, Rb, and Cs forms are active towards the dehydrogenation of isopropanol to give acetone.

The oxidation of benzyl alcohol on various zeolites has been studied[145,146]. In the presence of decationated type Y zeolite benzaldehyde, benzoic acid, benzyl ether, and CO_2 are formed[145]. Hydrogen treatment of the catalyst at 500° lowers its activity towards the oxidation by 60%. The addition of pyridine to the reaction mixture lowers the overall conversion of the benzyl alcohol, whereas the addition of water increases the yield of benzyl ether and lowers the yields of the oxidation products. On the Cu(II)Y zeolite the main products are benzaldehyde, CO, and CO_2.[146] The kinetic order of the reaction is unity for both oxygen and alcohol. The active centres are thought to be Cu(II) cations located in large zeolite holes. A recent patent[148] describes the oxidation of benzyl alcohol to benzaldehyde on type X and Y zeolites containing transition metal cations. The addition of initiators (peroxides, halides, etc.) to the reaction mixture is shown to increase the yield of benzaldehyde.

The oxidation of hydrogen sulphide on zeolites was first reported[24] in 1961, but detailed studies of this reaction were published much more recently[149–152]. It has been shown by ESR that when H_2S is adsorbed on NaX zeolite at room temperature the addition of oxygen leads to the formation of chain radicals [$^{\cdot}S-(S)_x-S^{\cdot}$ and $HS-(S)_x-S^{\cdot}$] and ion radicals (O_2^-, SO_2^-, and SO_3^-), which take part in the oxidation reaction[149]. According to the authors the high catalytic activity of NaX zeolite is due to the very strong deformation of the H_2S molecule after adsorption, and to the ease with which an electron can be transferred with H–S bond breaking. Lin and Lunsford[150] studied the interaction of H_2S with oxygen on MgO, amorphous alumina–silica, NaY, and MnNaY. On the MgO surface S^-, S^{2-}, and sulphite ions are formed during the oxidation. On NaY zeolite hydrogen sulphide dissociates with formation of elemental sulphur; the addition of Mn(II) ions to the zeolite increases the formation of sulphur. On an amorphous alumina–silica surface the rate of oxidation of H_2S is negligibly small.

Chabazite tuffs of various compositions are very active towards the oxidation of hydrogen sulphide[151]. The high selectivity of the reaction for sulphur (>98%) in the presence of a large excess of oxygen (15-fold excess over stoichiometry) is specially noteworthy. The formation of SO_2 among the reaction products begins after a definite induction period, suggesting that this compound is formed by consecutive reactions. It has been shown[152] that the Mn(II)Y zeolite catalyses the oxidation of SO_2 at room temperature to the sulphate ion (strongly bound in the zeolite micro-pores). As the dehydration temperature of the catalyst is raised the Mn^{2+} cations migrate into less accessible sites, with a loss of activity.

In the oxidation of methyl mercaptan NaX zeolite is more active than NaY, and Na-mordenite is practically inactive[153]. The activity of the zeolite has been shown to be related to the density of the cations in the elementary cell. The optimum reaction temperature is 450°; at higher temperatures the degree of conversion increases, but the selectivity of the reaction becomes unacceptably low.

VII. CONCLUSIONS

It is clear from the results considered here that zeolite catalysts have a high activity towards the oxidation of various organic or inorganic compounds. The selectivity of the process, the course of the oxidative transformation, and the specific features of the reaction are determined by the structure of the zeolite, by the state of oxidation of the transition metals, and by the nature and concentration of the ion-exchange cations. Clarification of the activation mechanism of molecular oxygen and of the hydrocarbon on the zeolite surface as a function of the zeolite composition and structure should make a valuable contribution to our understanding of the mechanism of catalytic oxidation.

Oxidation on oxide catalysts may involve both the oxygen contained in the catalyst and oxygen adsorbed from the gas phase[154–157]. In the case of zeolite catalysts the oxygen in the skeleton is very strongly bound[158,159], and isotope exchange between the skeleton oxygen and oxygen from the gas phase in NaX and NaY zeolites cannot take place below 600°. The existence of strongly bound oxygen, adsorbed from the air during heat treatment of decationated type Y zeolite and retained after vacuum heat treatment at 550°, has also been reported[160–162]. The correlation between the number of molecules of chemisorbed oxygen and the amount of cation radicals formed suggests the involvement of oxygen in this process as a reactant[162]; the observation that oxidation properties are confined to dehydroxylated surfaces of decationated zeolites has led to the conclusion[163] that oxygen chemisorption occurs on anion and cation lattice vacancies.

Strong oxidation–reduction centres have been detected on zeolite surfaces in an ESR study of the adsorption of various organic compounds[164–166]. The adsorption interaction of naphthalene molecules with a Na-faujasite surface to give a donor–acceptor charge transfer complex suggests[167] that NaX and NaY zeolites can retain (after vacuum heat treatment) strongly bound oxygen which is responsible for the oxidation properties of these zeolite surfaces. The important contribution of chemisorbed oxygen to the oxidation properties of mordenite is stressed also in Refs.168–172.

The formation of oxygen anion radicals by adsorption on different cationic forms of faujasites has been reported[173-183]. In most cases the ESR signals from the oxygen anion radicals are observed after irradiating the sample with γ-rays, X-rays, or u.v. light. However, on the Li, Na, Ti, and Pd forms of type Y zeolite the oxygen anion radicals are formed by adsorption of oxygen on vacuum heat-treated samples[179-184]. A thermo-desorption study has shown[185] that oxygen is adsorbed in different amounts and in different states on the Mn, Co, Ni, and Cr forms of type Y zeolite. On CuY zeolite (an active oxidation catalyst, which adsorbs large amounts of oxygen) five different states of adsorbed oxygen, with different reactivities, have been detected[186]. Inactive O^{2-} oxygen, which does not take part in oxidation reaction, is also present on CuX zeolite[187].

The catalytically active oxidation centres in zeolites have been identified as associated groups of transition metal atoms coordinated by non-lattice oxygen[119-124]. The adsorption and catalytic properties of isolated ions in the zeolite are quite different from those of an ion pair bound by a bridging oxygen atom. Measurements by γ-resonance spectroscopy have shown the existence of this type (M–O–M) of cation pair[45,83]. The oxidation of simple molecules (CO, H_2) on these centres is assumed[156,188] to involve a collision mechanism,

$$M^{(n+1)+}—O—M^{(n+1)+} + H_2(CO) \rightarrow 2M^{n+} + H_2O(CO_2),$$

followed by oxidation of the transition metal ions (M^{n+}) by oxygen.

The oxidation of low-molecular-weight hydrocarbons on zeolites yields mainly deep oxidation products; zeolites containing transition metals are the most active towards this reaction. Therefore the reactivity of oxygen is often discussed in terms of this reaction. With naphthene and alkylaromatic hydrocarbons oxidative dehydrogenation takes place in parallel with the deep oxidation. However, whereas the zeolites containing transition metals are the most active towards the oxidation of low-molecular-weight hydrocarbons, Na faujasites show a high activity in the deep oxidation of cyclohexane, and in this case the introduction of transition-metal cations favours oxidative dehydrogenation with formation of benzene[62,73].

Unlike the faujasites, the Na forms of various narrow-pore zeolites catalyse the oxidative dehydrogenation of cyclohexane with formation of cyclohexene[84,88]; the Na forms of various zeolites are active also in the oxidative dehydrogenation of iso-pentylenes[60] and ethylbenzene[100]. However, whereas the faujasites have a lower selectivity than the narrow-pore zeolites for the formation of styrene, in the oxidative dehydrogenation of iso-pentylenes the selectivity of the Na faujasites is greater than that of narrow-pore zeolites in the Na form.

Thus, though the Na forms of faujasites have no weakly bound lattice oxygen[158] and adsorb very much less oxygen than zeolites containing transition metals[185,186], they can nevertheless catalyse the oxidative dehydrogenation of iso-pentylenes, cyclohexane, and ethylbenzene. This can be explained by postulating a difference in behaviour towards oxygen between a zeolite surface covered with an adsorbed hydrocarbon and a pure zeolite surface. Alternatively, the reaction can be assumed to involve the formation of carbon–oxygen intermediate complexes with oxygen from the gas phase: in this case the course of the reaction should be determined mainly by the interaction between the zeolite and the hydrocarbons.

Thermo-desorption studies have demonstrated the strong dependence of the adsorbate–absorbent interactions on the structure and composition of the zeolite, and on the nature of the hydrocarbon[61,89,106]. Thus, in the case of cyclohexane and ethylbenzene the low selectivity of the faujasites towards the oxidative dehydrogenation reaction stems from the strong adsorption of these hydrocarbons, which favours deep oxidation. The more selective, narrow-pore zeolites adsorb neither ethylbenzene[106] nor cyclohexane[89]. On the other hand, 2-methylbut-2-ene is adsorbed both on faujasites and on narrow-pore zeolites[61]. However, in this case the diffusion of the hydrocarbon in the narrow-pore zeolite is slower than in the faujasite, as shown by the relative values of the effective diffusion coefficient. This may also explain the greater activity of the narrow-pore zeolites towards the deep oxidation of 2-methylbut-2-ene, whereas the faujasites show more selectivity towards the formation of isoprene. Furthermore, as the ionic radius of the alkali metal cation increases, the rate of the deep oxidation of 2-methylbut-2-ene also increases, and the selectivity towards isoprene decreases, possibly as a result of the obstacles to the diffusion of the hydrocarbons in the zeolite Y pores resulting from the presence of large cations.

Thus, our survey of published data on the oxidation of various compounds on zeolites from the standpoint of the influence of the structure and state of the crystalline aluminosilicates on the course of the reaction has revealed some interesting features. The similarity in size between the zeolite pores and the oxidisable molecules gives rise to large changes in the selectivity of the reaction for a particular product from quite small changes in the ratio of these two sizes. The possibility of controlling the course of the transformation of a given hydrocarbon towards the formation of different products by varying the structure and the composition of the zeolite is very attractive. This combination of flexibility and selectivity suggests many potential applications of zeolite reactions in the oxidative transformation of hydrocarbons.

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Some Problems in the Theory of Solid Electrolytes

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Modern theoretical views on solid electrolytes (i.e. solids whose ionic conductivity is anomalously high) are reviewed, and various mechanisms for the creation of disorder in one of the ionic sublattices are analysed, together with schemes for the phase transitions to the superionic state and with the dependence of the characteristics of these transitions on the parameters of the crystal and on the charge transfer phenomena in the solid electrolyte. Problems in the microscopic description of ionic transport in solid electrolytes are examined, and the theoretical foundations of the experimental methods used to study the properties of solid electrolytes are discussed.

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I. INTRODUCTION

In recent years solid electrolytes have increasingly claimed the attention of researchers (physicists, chemists, materials scientists) as well as of technologists, engineers, and system designers[1-11]. One of the most important features of solid electrolytes (their anomalously high ionic conduction) can be exploited at temperatures well below the melting point of the material. For example, whereas the ionic conductivity of "normal" solids at room temperature is not greater than 10^{-7}–10^{-8} Ohm^{-1} m^{-1}, that of "good" solid electrolytes is approximately 10 Ohm^{-1} m^{-1} at the same temperature, i.e. it is similar to the conductivity of melts and of concentrated (liquid) solutions of electrolytes. Thus materials of this type can be said to have "hybrid" properties, combining the conductivity of a melt or of a liquid solution with the mechanical strength and elasticity of a solid.

Solid electrolytes (also called "superionic conductors") can be arbitrarily classified into various types, depending on the magnitude of their ionic conductivity and on their structural features.

The first type includes crystals in which one of the sublattices (cation or anion) is structurally disordered. Many (several tens) of these compounds have already been discovered and studied, and their number is increasing[4,7,11]. The most typical example of this type of solid electrolyte is the compound $RbAg_4I_5$, with a room-temperature conductivity (due to the disordered Ag^+ cations) of ~25 Ohm^{-1} m^{-1}. This is 16 orders of magnitude higher than the ionic conductivity of common salt at the same temperature.

Another type of solid electrolyte includes substances which owe their high ionic conductivity to a high concentration of impurity ions able to activate the structural disorder. For example, if CaO is added to the ZrO_2 lattice the Ca^{2+} ions distribute themselves over the Zr^{4+} sublattice, and the O^{2-} ions complete the oxygen sublattice. However, because of the difference in charge between Ca^{2+} and Zr^{4+}, oxygen vacancies must appear in the mixed crystal, leading to disorder in the oxygen sublattice. These compounds are impurity solid electrolytes, or solid electrolytes with impurity-induced disorder. Examples are provided by the MO_2–M'O series of compounds (where M = Zr, Hf, Ce, and M' = Ca, Sr, Ba), whose ionic conductivity (due to oxygen ions) is ~1–10 Ohm^{-1} m^{-1} at 1000–1500°.

Lastly, amorphous glassy solids with a measurable ionic conductivity due to the presence of electrically active impurities[12,13], and ion-exchange resins, are also occasionally classified among solid electrolytes.

Most of the solid electrolytes with structural disorder show, at some characteristic critical temperature, a discontinuous change in ionic conductivity by a large factor (even by several orders of magnitude). Above this critical temperature the crystal is in a state of high ionic conductivity, and behaves as a solid electrolyte. In other words, we have a rational method of identifying superionic crystals among all the known crystalline compounds. Below their critical temperature (i.e. in their dielectric phase) these materials behave as "normal" crystals, and above their critical temperature they are converted into a qualitatively different state: the superionic (electrolyte) phase.

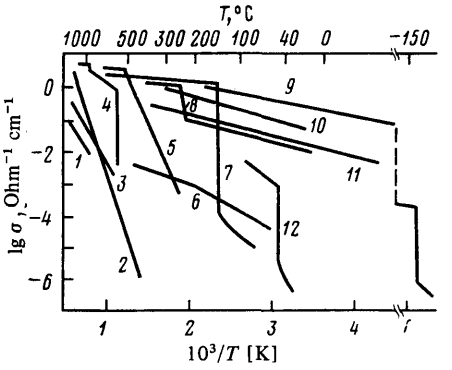


Figure 1. Temperature dependence of the conductivity of some solid electrolytes[5]: *1*) ThO_2–Y_2O_3, *2*) CaF_2, *3*) ZrO_2–CaO, *4*) Li_2SO_4, *5*) PbF_2, *6*) CeF_3, *7*) AgI, *8*) Ag_3SI, *9*) $RbAg_4I_5$, *10*) $Ag_6I_4WO_4$, *11*) Na–β-Al_2O_3, *12*) Ag_2HgI_4.

Unlike the superionic crystals, solid electrolytes with disorder due to impurities do not usually show a discontinuity in the temperature dependence of ionic conduction, though anomalies in this dependence may arise from phase transformations resulting in impurity redistribution.

The structure and the ionic conductivity of solid electrolytes of both these types are fully discussed in Refs.1–11. Therefore we shall not dwell on this set of problems, except to mention that the temperatures at which

solid electrolytes of the first class become good ionic conductors are usually much lower than those for the second class, and often even lie below room temperature. High ionic conductivity (≥ 1 Ohm^{-1} m^{-1}) is observed in a temperature range of over 1500 K, which includes all the known solid electrolytes: some examples are shown in Fig.1.

The electronic conductivity of solid electrolytes is usually much lower (by several orders) than their ionic conductivity, though it plays an important role in some materials. The theory of electronic conduction is dealt with in Refs.14–16, and will not be discussed here.

The problems in the behaviour of solid electrolytes lie at the "junction" of solid-state physics, crystallography, solid-state chemistry, and electrochemistry. By exploiting the wide range of experimental approaches offered by all these disciplines a very comprehensive fund of information (both specific, and generalised) has been generated. The aim of this review is to present some new theoretical concepts in the science of solid electrolytes and to discuss the theoretical foundations of the physicochemical methods used in their investigation.

II. THERMODYNAMICS OF SOLID ELECTROLYTES

The distinguishing feature of all solid electrolytes, which is ultimately responsible for their anomalously high ionic conductivity, is the presence of disorder (full, or partial) in one of the crystal sublattices. In the superionic crystals, for example, this disorder consists in the random distribution of the ions of one kind over the interstitial positions, whose number in these compounds is usually greater than the number of disordered ions. Because the relevant activation energy is very small, the interstitial ions have a very high mobility. In other words, the dynamic effect (anomalously high ionic conductivity) is unambiguously related to a thermodynamic effect (lattice disorder). The system can be described in terms of the somewhat arbitrary concept of an "ionic liquid" pervading a rigid crystalline skeleton consisting of ordered ions, analogous to the concept of an electronic liquid in metals+.

The most important problem in the thermodynamics of solid electrolytes is to explain and to describe quantitatively the sudden disordered ("melting") of one of the crystal sublattices. The formation of disorder is accompanied not only by a discontinuous increase in ionic conductivity but also by other anomalous effects in the temperature dependence of various thermodynamic and kinetic parameters[17,22].

The discontinuity in the number of highly mobile ions in interstitial positions is a phase transformation of the first kind. This transition may be produced in a number of ways, depending on the properties of the sublattice which remains rigid. In particular, the rigid sublattice may be quite unaffected by the disorder transition, or it may undergo secondary structural changes. In this case collective interactions in the system of crystal defects can be expected to play a major role. The theory of the disordering of one sublattice through collective interactions while the other sublattice remains unchanged has been developed by many workers[23–32]. However, there are crystals in which the disordering of one sublattice is accompanied by a rearrangement (polymorphic change) in the other sublattice which may have an important effect. The case of negligible interaction in the defect system, such that the disorder is induced exclusively by the lattice rearrangement, is analysed in Ref.33 (see also Ref.34); several special features of phase transitions involving disorder with comparable thermodynamic contributions from both factors are discussed in Ref.35.

One special feature of the thermodynamic behaviour of solid electrolytes is the possibility of forming domain structures. Some of the problems associated with domain formation are discussed in Refs.36–39.

1. Structural Disorder Induced by Lattice Rearrangement

Structural disorder in the absence of collective interactions in the defect system, and due entirely to a polymorphic transition, is the simplest to describe mathematically[33].

The traditional treatment of polymorphic changes in crystals relates these transitions to changes in the vibrational (phonon) spectrum of the solid[40,41]. Thus, it is assumed that the contribution of the phonon subsystem to the free energy increases with the temperature of the crystal, so that at some temperature $T_{tr}^{(p)}$ the transition of the crystal into a higher-energy modification (with "dumping" of the lattice vibration energy) becomes thermodynamically favourable.

However, if the polymorphic transition is accompanied by a substantial amount of disordering of one of the sublattices it is reasonable to assume that the thermodynamics of the process will be determined predominantly by the disordering process, with a much smaller contribution from the changes in phonon spectrum. In other words, polymorphic transitions in one sublattice may be induced by disorder in the other sublattice.

We shall use as our starting point some standard thermodynamic expressions from the theory of ionic crystals[2,3,42]. The free energy F of the crystal can be written as the sum

$$F = F^{(0)} + F^{(d)}, \qquad (1)$$

where $F^{(0)}$ is the free energy of the ideal (defect-free) crystal, and $F^{(d)}$ is the free energy resulting from the presence of disorder. The quantity $F^{(d)}$ can be expressed as

$$F^{(d)} = wn - T \ln \left\{ \frac{N_2!}{(N_2 - n)!\, n!} \frac{N_1!}{(N_1 - n)!\, n!} \right\} - nT \ln \chi, \qquad (2)$$

where N_1 and N_2 are the numbers of interstitial sites and of lattice sites per unit volume respectively, n is the number of ions per unit volume transferred from lattice sites to interstitials (and thus giving rise to Frenkel' defects in the crystal), w is the energy of formation of one defect#, T is the absolute temperature (expressed in energy units), and χ is a quantity related to the entropy of formation of one defect. In the simplest model $\chi = (\omega_2/\omega_1)^3$, where ω_1 and ω_2 are the vibration frequencies of the disordered ions in the interstitial sites and in the lattice sites respectively. The concentration n corresponding to thermodynamic equilibrium is defined by the condition of minimum disorder free energy: $\partial F/\partial n = 0$ [since $F^{(0)}$ is not a function of n]. Differentiating Eqn.(2), and using the expression

$$\frac{d}{dz} \ln z! = \ln z, (z \gg 1),$$

+For example, in $RbAg_4I_5$ the ionic liquid is formed by the disordered Ag^+ ions, and the rigid sublattice by the Rb^+ and I^- ions; in solid electrolytes with impurity disordering the "liquid" can consist, in principle, of vacancies.

#We can allow for effects associated with changes in volume of the crystal by replacing w by h (the enthalpy of formation of one defect).

we obtain the following expression for n:

$$n^2/(N_2-n)(N_1-n) = \chi \exp(-w/T) . \quad (3)$$

Assuming N_1 to be substantially higher than N_2 (as in the great majority of solid electrolytes) we can simplify Eqn.(3) to

$$x^2/(1-x) = \nu \exp(-w/T) , \quad (4)$$

where $\nu = \chi N_1/N_2$, and $x = n/N_2$ is a dimensionless concentration ($0 < x < 1$) used as a quantitative description of the degree of disorder. Using Eqn.(4) we can rewrite Eqn.(2) for $F^{(d)}$ as

$$F^{(d)} = N_2 T[\ln(1-x) - x] . \quad (5)$$

It follows from (3) and (4) that the function $x(T)$ increases monotonically with T from $x = 0$ at $T = 0$ to the value $x = x_\infty$ formally corresponding to the limit at $T = \infty$ and given [according to Eqn.(4)] by the expression

$$x_\infty = -\nu/2 + (\nu^2/4 + \nu)^{1/2} .$$

Hence, and using Eqn.(5), we find that $F^{(d)}$ decreases monotonically as T increases, with $F^{(d)} = 0$ at $T = 0$ and $F^{(d)}$ varying linearly with T for $T \gg w$.

Let us now consider two crystalline modifications (α and β), having free energies $F_\alpha(T)$ and $F_\beta(T)$. The modification having the lower free energy is present when the system is in thermodynamic equilibrium. As the temperature changes, the functions $F_\alpha(T)$ and $F_\beta(T)$ change at different rates, and the cross-over temperature (when $F_\alpha = F_\beta$) corresponds to the phase transition between the α and β modifications. This transition causes a rearrangement of the crystal lattice (polymorphic change) accompanied by a sudden change in the degree of disorder.

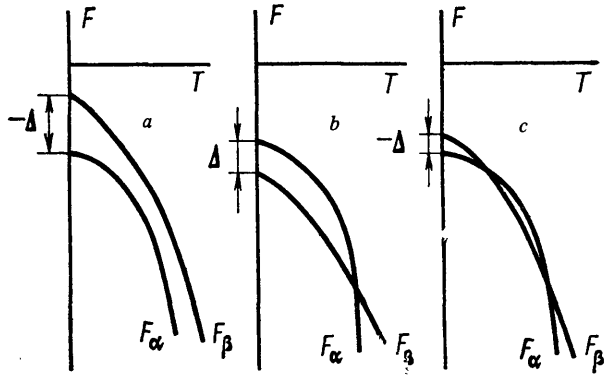


Figure 2. Idealised temperature dependences of the free energy F for α and β modifications: (*a*) no transitions, (*b*) single transition, (*c*) double transition.

The condition $F_\alpha = F_\beta$ can be written, using Eqn.(1),

$$F_\beta^{(d)} - F_\alpha^{(d)} = N_2\Delta , \quad (6)$$

where, by definition, $N_2\Delta = F_\alpha^{(0)} - F_\beta^{(0)}$, and the quantity Δ in our case is approximately independent of T and is determined by the difference in internal energy between the α and β crystalline modifications. The different mutual dispositions of the $F_\alpha(T)$ and $F_\beta(T)$ curves which are possible according to Eqns.(5) and (6) are shown in Fig.2. Case *a* corresponds to the absence of phase transitions, the crystal remaining in the α modification at all temperatures. In case *b* the low-temperature α modification is converted into the high-temperature β modification at the intersection point. Case *c* corresponds to two polymorphic transitions in succession ($\alpha \to \beta \to \alpha$, or bitransition).

From Eqns.(4)–(7) we can obtain a system of three equations defining the polymorphic phase transition temperatures $T_{tr}^{(p)}$ and the concentrations x_α and x_β of the interstitial ions before and after the transition:

$$T_{tr}^{(p)}\{\ln[(1-x_\beta)/(1-x_\alpha)] - (x_\beta - x_\alpha)\} = \Delta \quad (7)$$

$$x_\alpha^s/(1-x_\alpha) = \nu_\alpha \exp(-w_\alpha/T_{tr}^{(p)})$$

$$x_\beta^s/(1-x_\beta) = \nu_\beta \exp(-w_\beta/T_{tr}^{(p)}) , \quad (8)$$

Using Eqns.(5) and (6), the heat of the phase transition for a single particle is given by the expression

$$Q_p = \Delta + w_\alpha x_\alpha(T_{tr}^{(p)}) - w_\beta x_\beta(T_{tr}^{(p)}) , \quad (9)$$

and the specific heat of the disordering process ΔC for the α and the β modifications is

$$(\Delta C)_{\alpha,\beta} = w_{\alpha,\beta}x_{\alpha,\beta}(1-x_{\alpha,\beta})/T^2(2-x_{\alpha,\beta}) . \quad (10)$$

A detailed analysis of the conditions leading to single and to double transitions (bitransitions) is given in Ref.33, together with expressions for the corresponding transition temperatures.

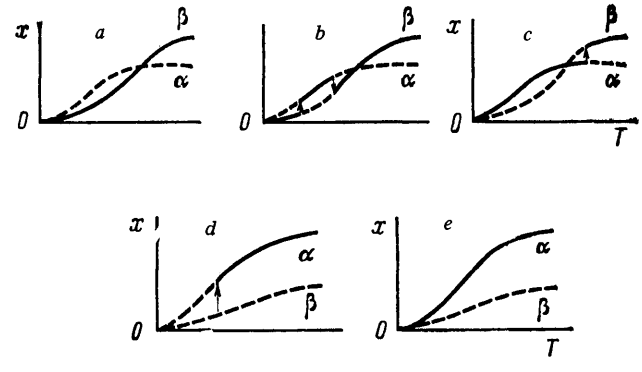


Figure 3. Possible temperature dependences of the degree of disorder $x_{\alpha,\beta}$, and schematic representation of the phase transitions for different relative values of the parameters Δ, $w_\alpha < w_\beta$, ν_α, and ν_β;[33] the full lines show the realisable situations, the arrows show transitions between these situations.

These expressions for the degree of disorder x as a function of temperature with allowance for polymorphic ($\alpha \rightleftharpoons \beta$) transitions are not trivial: different types of relationship are shown in Fig.3. We should stress that the relative amounts of disorder, and therefore also other characteristics of the solid electrolytes, can change by large amounts.

2. Structural Disorder Induced by Defect Interactions

We shall now consider how collective interaction between defects can be incorporated into a general thermodynamic scheme for describing the behaviour of the crystal.

Interstitial ions and the empty sites which they leave behind (vacancies) can interact both among themselves and with members of the other group (cross-over interaction), the total number of interacting pairs being proportional to n^2 in the case of $n \gg 1$. As a result, if in the absence of interactions the internal energy E of the system of n defects is $E = wn$, allowing for the collective interactions gives

$$E = wn - \frac{\lambda}{2}\frac{n^2}{N_a} ,$$

where λ is a phenomenological constant whose sign and value are determined by the nature of the inter-particle (including indirect) interactions in the ensemble of interstitial ions and vacancies. The case of $\lambda > 0$ corresponds to effective attraction, $\lambda < 0$ to repulsion.

An analysis of the specific interactions which contribute to λ is beyond the scope of this review. We shall only stress that contribution to effective attraction is possible not only from self-consistent Coulombic interactions[43] but also from the elastic deformations accompanying the formation of defects in the crystal[44], and from the changes in vibrational spectrum of the crystal predicted by second-order perturbation theory[45].

Replacing wn in Eqn.(2) by the corrected expression for E, and using the condition $\partial F^{(d)}/\partial n = 0$, we obtain instead of Eqn.(4) the equation of state[27-29]

$$x^2/(1-x) = \nu \exp[-(w-\lambda x)/T] \quad . \qquad (11)$$

The average field approximation used in the derivation of (11) is equivalent to the standard Bragg–Williams approximation in the theory of alloys[46] or to the Curie–Weiss approximation in the theory of magnetism[47]. Effectively the same approximation is used to describe regular solutions, adsorption with inter-particle interactions[48,49], the properties of liquid crystals[50], etc.

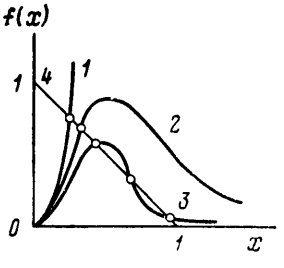


Figure 4. Graphical solution of Eqn.(11) ($f(x) = x^2\nu^{-1} \exp[(w - \lambda x)/T]$): *1*) for $\lambda = 0$, *2*) $0 < \lambda < w$, *3*) $\lambda > w$, *4*) is the $(1 - x)$ straight line.

Let us now consider, as in Refs.27 and 28, the thermodynamic behaviour of the system. If $\lambda = 0$ Eqn.(11) reduces to (4), and under these conditions (as well as for $\lambda < 0$) Eqn.(11) has only one solution (Fig.4). However, as Fig.4 shows, for large positive values of λ Eqn.(11) has three solutions $\{x_1 \leq x_2 \leq x_3\}$ in the range $0 \leq x \leq 1$. If the equation of state has only one solution, the free energy at a fixed value of T will have one minimum at the value of x corresponding to this root (Fig.5). In the case of three roots the function $F(x)$ has two minima (at the points x_1 and x_3) and one maximum (at the point x_2). The crystal is found in the state (x_1 or x_3) corresponding to the lower of the two minima in $F(x)$; the state x_2 corresponds to a local maximum in $F(x)$ and therefore is unstable.

Changes in T alter the shape of the $F(x)$ curve, and at a particular temperature $F[x_1(T)]$ becomes equal to $F[x_3(T)]$. This indicates a phase transition of the first kind which makes the parameter x (the degree of disorder) change discontinuously from x_1 to x_3 (or from x_3 to x_1). These phase transitions can arbitrarily be classified into weak or strong[27]. Weak transitions are those in which the jump in the value of x is small ($x_3 - x_1 \ll 1$); the strong transitions correspond to $x_1 \ll 1$ and $x_3 = 1 - \varepsilon$, with $\varepsilon \ll 1$. From the condition $F[x_1(T)] = F[x_3(T)]$, and using the equation of state (11), we obtain the following expression for the transition temperature in the two cases:

$$T_{tr}^{(w)} = (w - \lambda x_*)/\ln(\nu/\nu_*); \; T_{tr}^{(s)} = (w - \lambda/2)/(1 + \ln\nu) \qquad (12)$$

where $x_* = 2 - \sqrt{2}$, $\nu_* \equiv x_*^2/(1 - x_*)$, and therefore numerically $\nu_* = 2(\sqrt{2} - 1)$.

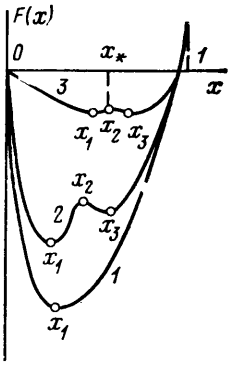


Figure 5. Idealised plots of F against x for different x and T: *1*) the equation of state has one solution, *2*) and *3*) the equation of state has three solutions $\{x_1, x_2, x_3\}$.

A full analysis of the variation of x with temperature for different values of the parameters of the system is given in Refs.28 and 29. Let us examine the main conclusions (Fig.6).

Firstly, gradual and continuous disordering of the initial sublattice with increase of T is possible, as in ordinary ionic crystals (Fig.6*a*), or a relatively slight discontinuity may occur, accompanied by a small jump in x (weak transition, Fig.6*b*).

Secondly, we can have a large jump from a state with a small x to a state with $x \cong 1$ (Fig.6*c*). As the temperature is increased still further the crystal remains in this state, or x may even decrease (compare Figs.6*a* and 6*c*). Physically, a decrease of x with increase of T implies that the state $x_3 > x_\infty$ is created and maintained if sufficiently strong interactions are present ($\lambda > 0$). As the temperature increases, the interaction is effectively "diluted", and at $\lambda/T \to 0$ the "defect gas" becomes ideal. Accordingly, in the state shown in Fig.6*c* the concentration of defects decreases as T increases, approaching (from above) the value $x = x_\infty$.

Thirdly, the system can show two successive transitions (Figs.6*d* and 6*e*). In the former case the second transition does not bring the crystal out of the superionic state,

whereas in the latter case we observe two genetically related phase transitions (bitransitions).

Lastly, the parameters of the system can be such ($\lambda > 2w$) that even at $T = 0$ the crystal is in the state with $x \cong 1$ (Figs. 6*f*, 6*g*, and 6*h*). In this case x decreases as T increases. We note that in the special case of $N_1 = N_2$ (see Ref. 23) double transitions cannot occur, and the temperature of the single transition in such a symmetrical system is given, irrespective of the magnitude of the jump in x, by the expression

$$T_{tr}^{sym} = (w - \lambda/2)/\ln \nu \ .$$

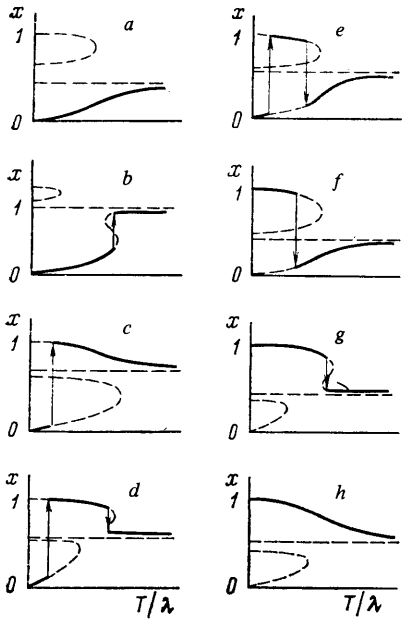


Figure 6. Idealised plots of the possible solutions of the equation of state and of the transitions between solutions: the full lines are realisable situations, the arrows are transitions between these situations.

The case of a collective interaction energy varying arbitrarily but monotonically with the defect concentration is discussed in Refs. 51 and 52, and more complex energy structures of the lattice points and of the interstitial sites are discussed in Refs. 31 and 53. In particular, in the presence of a small concentration of impurities ($c_{imp} = N_{imp}/N_2 \ll 1$) giving rise to interstitials with a different energy structure, the temperature of the strong transition is given[53] by the expression

$$T_{tr}^{(s,imp)} = T_{tr}^{(s)}[1 + c_{imp}/(\ln \nu + 1)] \ , \qquad (13)$$

where $T_{tr}^{(s)}$ is defined by Eqn. (12).

The dependence of the transition temperature T_{tr} on the pressure P is described by the Clausius–Clapeyron equation: $dT_{tr}/dP = (V - V')/(S - S')$, where V, V', S, and S' are the specific volumes and entropies of the states between which the transition is taking place. If the transition is strong the change in specific volume is $\nu_0 N_2$, where ν_0 is the "free volume" of formation of one defect. Assuming that the contribution of the polymorphic change to the thermodynamics of the transition is relatively minor, and using the expressions given above for $E(n)$ and $T_{tr}^{(s)}$, we obtain[54]

$$\frac{dT_{tr}^{(s)}}{dP} = \frac{N_2|v_0|T_{tr}^{(s)}}{w - \lambda/2} = \frac{N_2|v_0|}{1 + \ln \nu} \ . \qquad (14)$$

If the vibration frequencies ω_1 and ω_2 of the ions in interstitial positions and in lattice sites [which determine the parameter ν, see Eqns. (2) and (4)] have similar pressure dependences, the denominator of Eqn. (14) is independent of P, and the function $T_{tr}^{(s)}(P)$ can be treated as the sum of a linear and a quadratic term in P, since ν_0 varies linearly with P.

A model similar to the above has been used in Refs. 55 and 32 in a detailed analysis of weak transitions for particular values of the parameter N_1/N_2.

Attempts to apply scale invariance (scaling) concepts[56,57] to phase transitions in solid electrolytes are described in Refs. 58 and 59.

Spatially inhomogeneous regions (domains) in single crystals of solid electrolytes with structural disorder have been observed experimentally[36–39], and the theoretical possibility of thermodynamically stable inhomogeneities in solid electrolytes has been examined in detail[39,60].

3. Comparison of the Thermodynamic Theory of Disorder with Experiment

Theoretical models can be used to calculate the transition temperatures and the specific heats ΔC of the disorder, and these can be compared with experimental values. However, in order to find the excess specific heat associated with intrinsic disorder we must subtract from the measured value the specific heat of the defect-free crystal: this is usually done by choosing a particular model to describe the vibrational spectrum[61].

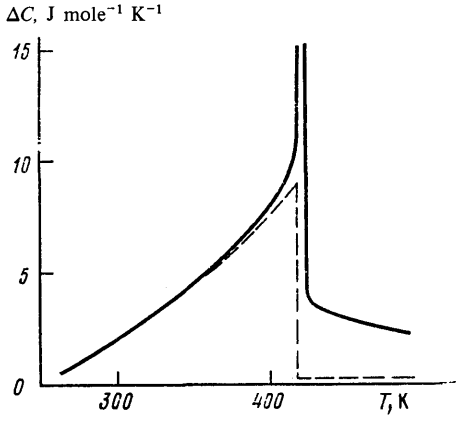


Figure 7. Experimental (full line) and theoretical (broken line) specific heat curves for the disorder in Ag_2S.[30]

The first attempt at interpreting experimental data[61] on the specific heat of superionic $RbAg_4I_5$ near the phase transition at $T_{tr}^{(s)} = 122$ K by the theoretical formulae which allow for defect interactions (see previous Section) is

described in Ref. 27. The same approach was later applied[30] to superionic crystals of AgI, $RbAg_4I_5$, Ag_2S, and others. As an example, the theoretical and the experimental ΔC curve for Ag_2S are compared in Fig. 7. The agreement is satisfactory for the low-temperature regions of the $\Delta C(T)$ curves, but above the transition temperature we note a substantial discrepancy, due no doubt to the polymorphic transition which takes place at the same time as the disorder transformation and for which no allowance is made in the calculation[62]. By comparing data on the excess specific heat of $RbAg_4I_5$ with calculations by a combined disorder and polymorphic transformation model a satisfactory description of the $\Delta C(T)$ curve has been obtained for $T > T_{tr}$ as well as for $T < T_{tr}$.

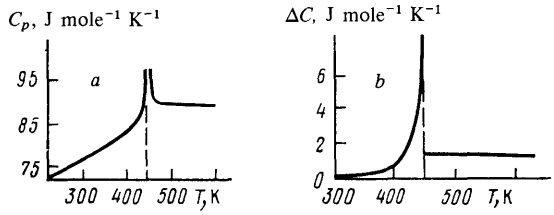


Figure 8. (*a*) Experimental plot of the full specific heat C_p, and (*b*) calculated plot of the specific heat of disordering ΔC in AgI.[34]

In Fig. 8 (taken from Ref. 34) we show some results on the excess specific heat of AgI, and in Fig. 9 we show a similar plot for Ag_2Se. The results were interpreted by the polymorphic transition model, using formula (10); the agreement between theory and experiment (for reasonable values of the adjustable parameters) is gratifying.

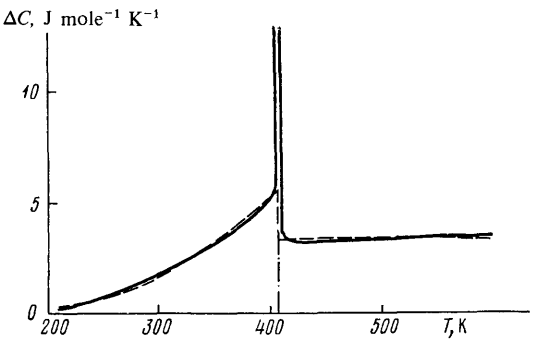


Figure 9. Experimental (full line) and theoretical (broken line) curves for the specific heat of disordering in Ag_2Se.[63]

Anomalies in the temperature dependence $\sigma(T)$ of the ionic conductivity of $RbAg_4I_5$ near the phase transition at $T = 209$ K (a "weak" transition) have been reported[64]. Measurements of the conductivity jump led to values of the thermodynamic parameters ($w = 5.6 \times 10^{-2}$ eV and $\lambda = 9.6 \times 10^{-2}$ eV) close to those previously calculated from specific heat data for the same compound but in a different temperature region ($w = 6 \times 10^{-2}$ eV and $\lambda = 10^{-1}$ eV).

Data[65] on the ionic conductivity of high-temperature solid electrolytes with the fluorite structure (CaF_2, SrF_2, $SrCl_2$) were compared[25,32] with theoretical models of disorder, and satisfactory agreement was obtained.

The dependence of the ionic conductivity of Na_2WO_4 crystals on temperature suggests[66] the existence of two (very close) phase transitions of the first kind accompanied by an increase and by a decrease in ionic conductivity respectively. This behaviour is consistent with the theoretically predicted bitransitions (see Fig. 6*e*). Further experimental evidence of the possible existence of bitransitions was obtained in a study[67] of the temperature dependence of Raman scattering in the solid electrolyte $Ag_{26}I_{18}W_4O_{16}$.

Calculations of the effect of impurities on the thermodynamics of disorder yield a qualitative explanation of changes in transition temperature along a series of isomorphous compounds (in particular, $RbAg_4I_5$, $K_{3/4}Rb_{1/4}$. $.Ag_4I_5$, and KAg_4I_5). Treating the K^+ ions as an impurity, we can calculate the transition temperatures by formula (13): the agreement between theory and experiment (see below) is satisfactory:

Compound	$RbAg_4I_5$	$K_{3/4}Rb_{1/4}Ag_4I_5$	KAg_4I_5
T_{tr}, K (exper)	122	134	137
T_{tr}, K (calc)	122	135.5	140

Experiments on the effect of pressure P on the phase transition temperature T_{tr} in solid electrolytes are reported in Ref. 68. For the compound AgI the function $T_{tr}(P)$ is accurately described by a straight-line dependence corresponding to a decrease in volume of the crystal by ~5.6% during the transition from the low-temperature to the high-temperature phase. In the case of the solid electrolyte $RbAg_4I_5$ we must retain the quadratic terms in P to describe the $T_{tr}(P)$ relationship. We note that the parameters needed to apply formula (14) are not yet known with sufficient precision.

III. BEHAVIOUR OF SOLID ELECTROLYTES IN AN EXTERNAL FIELD. TRANSPORT PHENOMENA

Transport phenomena can be treated by different approaches: one of them (the macroscopic approach) relies on the phenomenological equations of the thermodynamics of irreversible processes, the other (microscopic) relies on concrete microscopic models of the process of interest. The first approach requires very little detail, the properties of the system being described by the phenomenological parameters inserted into the theory. In the present state of development of kinetic models of homogeneous and heterogeneous charge transfer processes in solid electrolytes the phenomenological description offers the best (and sometimes the only) approach.

The electro-diffusion equations applied to transport phenomena in liquid electrolytes and in ionic crystals are based essentially on this phenomenological approach. The same equations (in most cases, unmodified) have been used also to describe the transport of current carriers in solid electrolytes[2-5]. However, solid electrolytes have a number of specific features which are ignored in the standard description, though they may play an important role. The present review is aimed specifically at those features.

The second approach, which should relate the phenomenologically chosen coefficients to the microstructural details and to the dynamic characteristics of the microscopic processes, is still in the formulation stage.

Some aspects of the study of micro-processes and some of the results obtained will be discussed in the following Section.

For relatively small deviations from equilibrium the transport properties of a system are closely related to its thermodynamic properties. Hence, in the phenomenological approach the flows of components (charge carriers) are proportional to the gradients of their electrochemical potentials, which can be obtained from the expression for the free energy F of the system.

For a solid electrolyte with structural disorder and exposed to an external electric field we can write, using the concepts discussed in previous Sections,

$$F(n_1, n_2) = E_1 n_1 + E_2(N_2 - n_2) + e\varphi(n_1 - n_2) - \\ - T \ln \left\{ \frac{N_1!}{(N_1 - n_1)!\, n_1!} \frac{N_2!}{(N_2 - n_2)!\, n_2!} \right\} , \quad (15)$$

where n_1 and n_2 are the concentrations of interstitial ions and of vacancies, E_1 and E_2 are the energies needed to force the ion into an interstitial and to remove it from a lattice site ($E_2 - E_1 = w$), and ϕ is the potential due to the electric field in the crystal. The quantities n_1, n_2, and ϕ usually depend on the spatial coordinates. In Eqn.(15) the terms which allow for changes in the vibrational frequencies due to disorder (vibrational terms) have been omitted to simplify the treatment, and collective interactions have been assumed to have a negligible effect ($\lambda = 0$). The expressions for the electrochemical potentials $\mu_{1,2} = \partial F/\partial n_{1,2}$ of the interstitial ions and of the vacancies are

$$\mu_1 = E_1 + e\varphi + T \ln[n_1/(N_1 - n_1)] \\ \mu_2 = -E_2 - e\varphi + T \ln[n_2/(N_2 - n_2)] . \quad (16)$$

Eqns.(16) can be used to describe both the equilibrium properties of a solid electrolyte in an electric field and the transport phenomena.

1. Equilibrium States in an Electric Field

The concentration distributions of interstitial ions and of vacancies n_1 and n_2 corresponding to thermodynamic equilibrium can be calculated from the conditions of constant chemical potentials and of "chemical equilibrium" ($\mu_1 + \mu_2 = 0$). From (16) we have

$$n_1 = n_0/[\gamma_1 + (1 - \gamma_1)\exp\psi]; \quad n_2 = n_0/[\gamma_2 + (1 - \gamma_2)\exp(-\psi)] . \quad (17)$$

In these expressions $\psi \equiv e\phi/T$, and $\gamma_{1,2} \equiv n_0/N_{1,2}$, where n_0 is the equilibrium concentration of defects in the absence of the electric field, given§ by Eqn.(3). In the limit of $\gamma_1 = \gamma_2 = 0$ Eqn.(17) reduces to the standard Boltzmann distribution: $n_{1,2} = n_0 \exp(\pm\psi)$. However, in the general case the concentrations $n_{1,2}$ are described by distributions of the Fermi type, and at the limit of $\psi \to \pm\infty$ the concentrations n_1 and n_2 reach their maximum allowed values N_1 and N_2. This result demonstrates the lattice saturation effect[69]: the concentrations of interstitial ions and vacancies have an upper limit defined by the specific properties of the crystal. In the simplest case the lattice saturation effect is due to purely structural limitations (the fact that the number of positions available to the ions in the crystal lattice is finite). In the more general case the effect reflects also the interparticle interactions, and the limiting value of $n_{1,2}$ is defined by the appropriate $n_{1,2}^{max}$ value (rather than by $N_{1,2}$), which is a characteristic parameter of the crystal.

§If the neglected terms associated with the entropy of formation of individual defects are retained in (15) and (16) the expressions (17) are unchanged, and the frequency factor χ occurs only in the equation for n_0.

It is interesting to consider the behaviour of $n_{1,2}$ and ϕ near the interface with allowance for the screening effect on the external field due to the redistribution of the charged particles. Within the self-consistent field approximation the potential distribution is given by an equation of the form

$$d^2\varphi/dz^2 = -\frac{4\pi}{\varepsilon_0} e[n_1(\varphi) - n_2(\varphi)] , \quad (18)$$

where z is the coordinate along the axis at right angles to the planar interface, ε_0 is the static dielectric constant of the crystal, and $e > 0$ is the electronic charge. Inserting into Eqn.(18) the Boltzmann distribution for $n_{1,2}$ we arrive at the standard self-consistent equation of the Gouy–Chapman and Debye–Hückel theories[70]. Integration of (18) after using (17) gives the electric field distribution $d\phi/dz$ and the integral charge Q_e of the surface (diffusion) layer. By differentiating the expression for Q_e with respect to potential we obtain the differential capacity C [70] of the diffusion layer:

$$-\frac{d\psi'}{dz} = \varkappa \operatorname{sgn}(\psi') \left[\frac{1}{\gamma_1} \ln \frac{n_0}{n_1} e^{-\psi'} + \frac{1}{\gamma_2} \ln \frac{n_0}{n_2} e^{\psi'} \right] \quad (19)$$

$$C = \frac{C_0}{2} \frac{\operatorname{sgn}\psi' \,[(n_1 - n_2)/n_0]}{\left[\gamma_1^{-1} \ln \frac{n_0}{n_1} e^{-\psi'} + \gamma_2^{-1} \ln \frac{n_0}{n_2} e^{\psi'} \right]^{1/2}} \quad (20)$$

where ψ' is the value of the potential ψ at the edge of the diffusion layer, $\kappa \equiv (8\pi e^2 n_0/\varepsilon_0 T)^{1/2}$, (where κ^{-1} is the Gouy or Debye length), $C_0 \equiv \varepsilon_0 \kappa/4\pi$, $\operatorname{sgn}(\psi') = 1$ for $\psi' > 0$ and $\operatorname{sgn}(\psi') = -1$ for $\psi' < 0$, and the $n_{1,2}$ values are given by Eqn.(17) with $\psi = \psi'$.

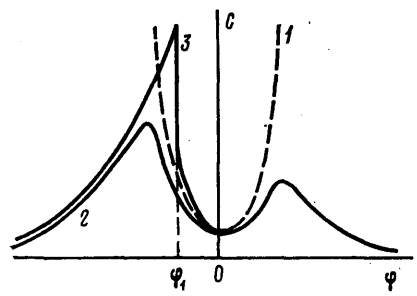


Figure 10. Plots of the diffusion layer capacitance against potential: *1*) $\gamma_1 = \gamma_2 = 0$, *2*) $1 > \gamma_2 > \gamma_1 > 0$, *3*) $\lambda_1 > 0$, $\lambda_2 = \lambda_{12} = 0$, $1 > \lambda_2 > \lambda_1 > 0$.

For $\gamma_1 \to 0$ and $\gamma_2 \to 0$ we obtain from Eqn.(20) $C = C_0 \cosh(\psi'/2)$, which corresponds to the capacity of the diffuse part of the double layer in liquid electrolytes (curve *1* of Fig.10). In the more general case the lattice saturation effect produces two asymmetric maxima in the $C(\psi)$ curve, and far from these maxima (for $|\psi| \to \infty$) we have $C = C_0/(\gamma_{1,2}|\psi|)^{1/2}$ [69] (see curve *2* of Fig.10). A formula similar to (20) is given in Ref.71 for the special case of $\gamma_1 = \gamma_2$. The unipolar model (in which charges of one sign only are redistributed in the field) corresponds to the limit $\gamma_2 = 1$ (or $\gamma_1 = 1$) in Eqns.(19) and (20). Expressions following from (19) and (20) in this model are given in Ref.72.

Thus, because of the lattice saturation effect the capacity of the diffuse part of the double layer in solid electrolytes is quite different from the analogous capacity in liquid

electrolyte systems. We should stress that the experimentally measured capacity is not determined only by the capacitance of the diffusion layer. The surface layer of the crystal may have properties different from those of the bulk (in particular, the energies of defect formation may be different). The influence of the surface layer on the distribution of space charge at the boundary between an ionic crystal and a vacuum is discussed in Refs.73 and 3.

To describe the boundary between a solid electrolyte and a metal we must also allow for the contribution from the fixed part of the double layer (the Helmholtz layer), as in the case of the boundary between a liquid electrolyte and a metal[70]. The effect of the Helmholtz layer, and detailed models of the two surface layers of ions in an ionic crystal, are fully described in Ref.3. We shall not dwell on the expressions obtained for the overall capacity: they are cumbersome, and they contain many parameters which have to be determined experimentally.

A novel effect, associated with the appearance of collective interactions in a crystal exposed to an electric field, is discussed in Ref.74. This effect consists in the stepwise, field-induced generation of disorder. It can be described mathematically as follows[74,75]. The chemical potentials $\mu_{1,2}$ corrected for collective interactions are given by the following expressions [instead of Eqn.(16)]:

$$\mu_1 = E_1 + e\varphi + T\ln n_1/(N_1 - n_1) - T\ln Z_1 - \lambda_1 n_1/N_2 - \lambda_{12} n_2/N_2$$
$$\mu_2 = -E_2 - e\varphi + T\ln n_2/(N_2 - n_2) + T\ln Z_2 - \lambda_2 n_2/N_2 - \lambda_{12} n_1/N_2 \quad (21)$$

In these expressions λ_1, λ_2, and λ_{12} describe respectively the interactions between interstitial ions, the interactions between vacancies, and the interactions between the two types of defect (with $\lambda = \lambda_1 + \lambda_2 + 2\lambda_{12}$); $Z_{1,2}$ are the vibrational partition functions of the ions in interstitials and in lattice sites (with $\chi = Z_1/Z_2$). As a result we obtain from (21) a system of two meshing equations for the dimensionless concentrations $x_{1,2} = n_{1,2}/N_2$ which is parametrically dependent on ϕ and on $x_0 = n_0/N_2$, where n_0 is the value of $n_1 = n_2$ in the absence of an electric field (depending on the difference $E_1 - E_2$ and on the ratio Z_1/Z_2).

The solution of this system over a given range of ϕ values is not unique, and this gives the possibility of phase transitions. The following physical explanation may be suggested. The field causes a redistribution of the charged particles, and the concentration of particles of one kind in the surface layer is increased. The collective interaction energy is itself a function of the concentrations of both kinds of particle. Since a high enough contribution from collective interactions can lead to phase transition, the field can also initiate phase transitions by varying the concentrations of interacting components. In particular, for one of the simplest cases ($\lambda_2 = \lambda_{12} = 0$, $\lambda_1 > 0$, $N_1 = N_2$) we obtain¶ from Eqn.(21)

$$\frac{x_1}{1-x_1} = \frac{x_0}{1-x_0}\exp\left[\frac{\lambda_1(x_1 - x_0) - e\varphi}{T}\right];$$
$$\frac{x_2}{1-x_2} = \frac{x_0}{1-x_0}\exp\left[\frac{e\varphi}{T}\right]. \quad (22)$$

Evidently, when $\lambda_1 > 4T$ the $x_1(\phi)$ curve has an S-shaped portion (see Fig.11), and therefore a change in ϕ must produce a discontinuous jump in x_1. The transition potential ϕ_1 and the discontinuity Δ_1 in the concentration x_1 at the transition are found to be[74]

$$e\varphi_1 = -T\ln(1-x_0)/x_0 + \lambda_1(1/2 - x_0) \quad (23)$$

$$(1+\Delta_1)/(1-\Delta_1) = \exp(\lambda_1\Delta_1/T). \quad (24)$$

¶The case of $\lambda_1 = \lambda_{12} = 0$, $\lambda_2 > 0$ can be treated in a similar way.

In other words, if the potential ϕ varies with the spatial coordinate we obtain a discontinuous change in the concentration x_1 by an amount Δ_1 at the coordinate for which $\phi = \phi_1$. Transitions of this type can give rise to an anomalous charge distribution in the surface layer. By using Eqn.(18) and the solution (22) it can be shown[74] that at high enough potentials an anomalous region of thickness z_* and properties different from those of the bulk material is formed near the surface (see Fig.12). Under these conditions the surface layer can be either enriched or depleted of interstitial ions, depending on the value of x_0, or of vacancies (in the case of $\lambda_1 = 0$, $\lambda_2 > 0$).

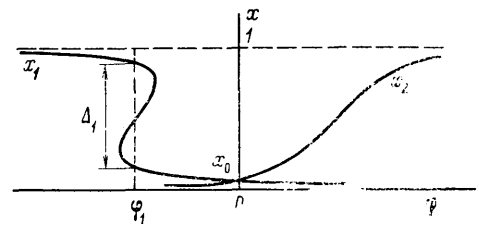


Figure 11. Plots of $x_1(\phi)$ and $x_2(\phi)$ for $\lambda_1 > 4T$ and $\lambda_2 = \lambda_{12} = 0$.

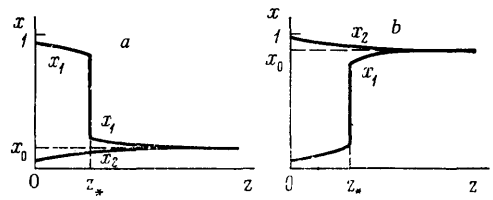


Figure 12. Distribution of x_1 and x_2 in the near-surface region for $\lambda_1 > 4T$ and $\lambda_2 = \lambda_{12} = 0$: (*a*) $x_0 \ll 1$, (*b*) $x_0 \cong 1$.

This effect (the production of a surface layer with anomalous properties whose thickness can be controlled by an applied potential) should be found in all physicochemical processes sensitive to charge distributions near phase boundaries. In particular, if the collective interactions play an important role, and the field can initiate a phase transition, the capacity of the diffusion layer changes suddenly when the transition potential ϕ_1 is reached (curve 3 of Fig.10). The effect can be observed also in studies of ionic surface conductivity, of optical properties of surfaces, and of the current–voltage characteristics of various interfaces (see below). We should stress that surface disorder induced by an electric field may occur also when thermal transitions are excluded by the values of the crystal parameters.

In addition to the surface disorder discussed in Ref.74, an external electric field applied to a crystal can induce disorder (and hence a jump in ionic conductivity) within the volume of the crystal. The theory of discontinuities in bulk ionic conductivity induced by an electric field was developed in Ref.76, and the first experimental data on this effect were reported in Ref.77.

2. Phenomenological Transport Equations

We shall now examine a solid electrolyte with structural disorder whose conductivity is caused by interstitial cations and cation vacancies. There is no difficulty in principle in generalising the discussion to more complex systems. According to the basic principles of irreversible thermodynamics the flows of components (i) can be expressed as[78,79]

$$i_{1,2} = \mp \frac{eD_{1,2}}{T} n_{1,2}(1 - n_{1,2}/n_{1,2}^{\max}) \nabla\mu_{1,2} \ , \qquad (25)$$

where the subscripts 1, 2 refer to interstitial cations and to vacancies, and $D_{1,2}$ are the diffusion coefficients, related to the mobilities $u_{1,2}$ by the Nernst–Einstein relationship $eD_{1,2}/T = u_{1,2}$. Using Eqn.(16) we obtain

$$i_{1,2} = \mp eD_{1,2}[\nabla n_{1,2} \mp eu_{1,2}n_{1,2}(1 - n_{1,2}/n_{1,2}^{\max}) \nabla\varphi] \ . \qquad (26)$$

In the region of $n_{1,2} \ll n_{1,2}^{\max}$ (where the lattice saturation effect is absent) the expressions (26) are indistinguishable from the standard expressions for the currents in systems with low carrier concentrations. Allowing for lattice saturation involves a modification to the transport equations[78,79].

In the absence of current the interstitial ions and the vacancies are in thermodynamic equilibrium†. The flow of current (in general) perturbs the equilibrium. Hence, terms describing the generation–recombination (i.e. the relaxation) processes of the carriers must be included in the transport equations. Thus, the full system of equations for calculating the distribution of the three quantities n_1, n_2, and the potential $\psi \equiv e\phi/T$ is

$$\frac{\partial n_1}{\partial t} = D_1 \frac{\partial}{\partial x}\left[\frac{dn_1}{dx} + n_1\left(\frac{n_1^{\max}}{n_1^{\max} - n_1}\right)^{-1}\frac{d\psi}{dx}\right] + q(n_1, n_2, \psi) \qquad (27)$$

$$\frac{\partial n_2}{\partial t} = D_2 \frac{\partial}{\partial x}\left[\frac{dn_2}{dx} - n_2\left(\frac{n_2^{\max}}{n_2^{\max} - n_2}\right)^{-1}\frac{d\psi}{dx}\right] + q(n_1, n_2, \psi) \qquad (28)$$

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi e^2}{\varepsilon_0 T}(n_1 - n_2) \ . \qquad (29)$$

The relaxation processes in the system are described by the function $q(n_1, n_2, \psi)$. In particular, starting from the law of mass action, and allowing for the lattice saturation effect, we arrive at

$$q = -k_1 n_1 n_2 + k_2(n_1^{\max} - n_1)(n_2^{\max} - n_2) \ ,$$

where $k_{1,2}$ are the rate constants for the recombination and the generation of the carriers. Under steady-state conditions (i.e. $\partial n_{1,2}/\partial t = 0$) the continuity of the total current ($i = i_1 + i_2$) follows from Eqns.(27) and (28).

The above system of non-linear equations is very complex and can only be solved by approximate methods. One of these methods, used in the solution of electro-diffusion problems in liquid electrolytes, is the boundary layer method[80–83], which relies on the fact that the problem includes a small parameter.

The size of the cell L is usually many orders of magnitude greater than the Gouy (or Debye) screening length κ^{-1}, and therefore we can (as in the case of liquid electrolytes) separate the space charge region of thickness l (comparable to κ^{-1}) from the region of electrical neutrality of thickness L, the size ratio of the two regions being $l/L \ll 1$.

In the electrically neutral region $n_1 = n_2$, and the system of three equations (27)–(29) reduces to the two equations (27) and (28) for the two unknowns $n_1 = n_2$ and ψ. Conversely, in the space charge region we can ignore those equations, and confine our analysis to Eqn.(29), by assuming that in this region the n_1 and n_2 concentration distributions are not perturbed by the flow of current. A detailed discussion of this type of problem is given in Ref.81. The equality $n_1 = n_2$ also allows the expression for q to be linearised to $q = (n_0 - n_1)/\tau$, where n_0 is the equilibrium concentration defined by Eqn.(3), and

$$\tau^{-1} \equiv 2k_1 n_0 + k_2[(n_1^{\max} - n_0) + (n_2^{\max} - n_0)]$$

is the reciprocal relaxation time, independent of $n_{1,2}$. Introducing the relaxation length $l_\tau \equiv (D\tau)^{1/2}$, where D is the smaller of the two values D_1 and D_2, we find that different relative values of L, l_τ, and l give rise to different cases, in which the behaviour of the system is qualitatively different:

1) $l_\tau \leqslant l \ll 1$, the fast relaxation case#;
2) $l \ll L \ll l_\tau$, the slow relaxation case;
3) $l \ll l_\tau \ll L$, the intermediate case.

We must stress that, although the above discussion has been aimed specifically at transport and relaxation processes involving carriers of two kinds, the limitation was not implicit in the use of separate electro-neutrality and space charge regions, or in the calculation of generation–recombination effects. In more complex systems several relaxation processes may be taking place simultaneously, and their role has to be analysed specifically for each particular case. Such an analysis is essential in studies of alternating-current processes in solid electrolytes, for example. Theoretical studies of this type are still insufficiently developed[2–5].

From Eqns.(30) and (31) the limiting current $i_{\lim}$ can be calculated directly. In the case of liquid electrolytes $i_{\lim}$ is determined under stationary conditions with only one type of current carrier (n_1, say), so that $n_1(L) = n_2(L) = n_0$, and at the electrode $n_1(0) = 0$. For the same conditions in solid electrolytes (assuming $q = 0$) we obtain[78,82,83]

$$i_{\lim} = i_D[(\gamma_1 + \gamma_2)/\gamma_2 + (\gamma_1 - \gamma_2)\ln(1 - \gamma_2)/\gamma_2^2] \ , \qquad (30)$$

where $i_D \equiv eD_1 n_0/L$. In the limit of $\gamma_{1,2} \to 0$ Eqn.(30) reduces to $i_{\lim} = 2i_D$, the familiar expression for a binary liquid electrolyte[70]. In general we see from Eqn.(30) that $i_{\lim} > 2i_D$, i.e. the lattice saturation effect increases $i_{\lim}$.

We note that allowance for relaxation processes in the linear approximation does not alter the general form of Eqn.(30) for $i_{\lim}$, and only involves re-normalisation of the i_D value.

An effect closely associated with transport phenomena is the development of a potential difference $\Delta\phi$ under open circuit by the application of a temperature difference ΔT between the electrodes. The thermo-electric power θ is defined as the limit

$$\lim_{\Delta T \to 0} \frac{\Delta\varphi}{\Delta T} = \theta \ .$$

If carriers of one kind only are mobile the parameter θ can be expressed, from the basic principles of the thermodynamics of irreversible processes, by the equation

$$\nabla\tilde{\mu} = \theta\nabla T \ ,$$

†The equilibrium concentrations under these conditions are defined by the condition $\mu_1 + \mu_2 = 0$ [see Eqn.(17)].

#In this case l_τ may differ from $(D\tau)^{1/2}$.

where $\tilde{\mu}$ is the electrochemical potential of the mobile carriers. The quantity $\theta = \theta_{hom} + \theta_{het}$ is divided into a homogeneous component $\theta_{hom} = -Q/Te$, where Q is the heat of transport of the ion§, and a heterogeneous component θ_{het}, associated with the temperature dependence of the contact potential differences at the interfaces. If the current is carried by singly charged cations, and local equilibrium is established at the phase boundaries, we can assume that the component θ_{het} is independent of T [84] and write

$$\theta = -Q/Te + \text{const} \quad .$$

Experimental determination of Q from the slope of the linear (θ, T^{-1}) plot yields values close to the activation energy for conduction of the mobile ions. This conclusion is consistent with calculations by the microscopic approach[85-87] (see Section IV).

From measured values of θ we can calculate the thermodynamic characteristics w and λ of the crystal, discussed in Section II. These values are found to agree with those obtained from measurements of the excess specific heat of the disordering process[63].

3. Transport Through a Phase Boundary

Theoretical descriptions of electrode processes are dependent on a correct model of the mechanism by which the current carriers are discharged at the phase boundary. In general, the partial currents i_1 and i_2 at the electrode depend on the carrier concentrations n_1 and n_2 at the discharge plane, and also on the electrode potential ϕ_0 and on the structure of the region adjacent to the electrode. The exact form of the kinetic relationship $i_{1,2} = i_{1,2}(n_1, n_2, \phi_0)$ is largely determined by the chosen microscopic model. The mathematical expressions describing the electrode process can also be used as boundary conditions for the phenomenological transport equations.

A detailed theory of ionic discharge phenomena at a phase boundary, including a solid electrolyte, is not yet available. It is reasonable, therefore, to apply to our system the general model of the slow discharge theory[70], developed for the boundary between a liquid electrolyte and a metal. However, the equations of this theory need some modification. When corrected for the lattice saturation effect and for the contribution of both interstitial ions (cations) and vacancies to the electrode process, the slow-discharge equations for the currents i_1 and i_2 at the electrode–solid electrolyte interface become

$$i_1 = i_{10}\left[\frac{n_1^{max} - n_1}{n_1^{max} - n_1^e}\exp(\beta_1\eta) - \frac{n_1}{n_1^e}\exp(-\alpha_1\eta)\right] \qquad (31)$$

$$i_2 = i_{20}\left[\frac{n_2}{n_2^e}\exp(\beta_2\eta) - \frac{n_2^{max} - n_2}{n_2^{max} - n_2^e}\exp(-\alpha_2\eta)\right] \quad . \qquad (32)$$

In these expressions i_{10} and i_{20} are the exchange currents of interstitial cations and cation vacancies respectively, η is the overvoltage ($\eta \equiv (\psi^0 - \psi^0_e) - (\psi' - \psi'_e)$, where ψ^0 and ψ' are the potentials in T/e units of the electrode surface and of the discharge plane¶ of the ions, $n^e_{1,2}(\psi'_e)$ are the equilibrium values (at $\eta = 0$, or $i_1 = i_2 = 0$) of the surface concentrations $n_{1,2}(\psi')$ which appear in (31) and (32); $\alpha_{1,2}$ and $\beta_{1,2}$ are the transport numbers for the cations and the vacancies ($\alpha_{1,2} + \beta_{1,2} = 1$). The presence of two different exchange currents (for ions and for vacancies) in Eqns.(31) and (32) with a common value of η follows from the principle of detailed balancing. Eqns.(31) and (32) can be used, with (27)–(29), to calculate the polarisation current–voltage characteristics of the system.

If the stationary currents are not large ($i_{1,2} < i_D$) we find that apart from their dependence on the relaxation characteristics (the relative values of l, l_τ, and L) the polarisation curves have similar shapes†, determined by Eqns.(31) and (32) with $n_{1,2}$ and $n^e_{1,2}$ values given by Eqn.(17) and η given by the equation

$$\psi^0 - \psi' = \frac{\varepsilon_0 d}{\varepsilon}\frac{d\psi}{dx}$$

(where d and ε are the thickness and the dielectric constant of the Helmholtz layer). This expression, which is used in the theory of the double layer[70], follows from the condition of continuity of the electrical induction at the phase boundary. An analysis of the system leads to the following conclusions:

1. In the low overvoltage region ($|\eta| \ll 1$) we find an ohmic portion $i = R^{-1}(\phi^0 - \phi^0_e)$, and the resistance of the reaction $R = T/e(i_{10} + i_{20})$ depends on the sum of the exchange currents.

2. In the "intermediate" overvoltage region Tafel's law is obeyed, and at fairly high overvoltages a new law sets in as a result of the lattice saturation effect. In particular, if $i_{10} \gg i_{20}$ and $\psi^0 > 0$ we have[88]

$$\ln i/i_{10} = \beta_1\psi^0 + a, \quad \psi^0 < \psi^0_* \qquad (33)$$

$$\ln i/i_{10} = \beta_1\delta(\psi^0/\gamma_2)^{1/2} + b, \quad \psi^0 > \psi^0_* \qquad (34)$$

where a and b are constants independent of ψ^0, $\delta = \kappa d\varepsilon_0/\varepsilon$, and the potential ψ^0_* of the transition between the laws (33) and (34) is given by

$$\psi^0_* = \ln(\gamma_2)^{-1} + \delta\left(\frac{1}{\gamma_2}\ln 2\right)^{1/2} \quad .$$

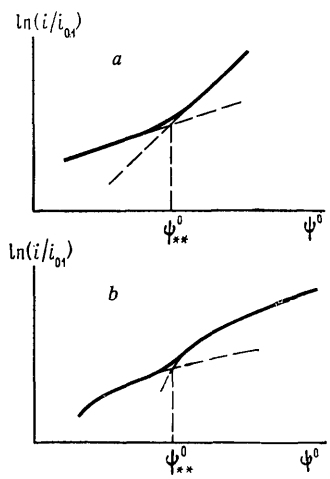


Figure 13. Transitions between different kinetic discharge regimes: (*a*) regimes corresponding to Eqn.(33), (*b*) to Eqn.(34).

§The component θ_{hom} is associated with the cross-over $L_{12} = L_{21}$ coefficient of the phenomenological transport equations of irreversible thermodynamics.

¶This plane is usually identified with the boundary of the diffusion layer (see Section III).

†In the limit of $\tau \to 0$ their shape is the same even for currents $i > i_D$.

3. A transition between different electrochemical reaction regimes is possible: from the discharge of interstitial ions ($i_1 \gg i_2$) to the discharge of ionic vacancies ($i_2 \gg i_1$), or *vice-versa*[82]. The transition may be between current–voltage characteristics of the Tafel type [Eqn.(33)] or of the type of Eqn.(34) (see Fig.13). The potentials of the transitions between regimes (ψ^0_{**}) are given (for $\psi^0 > \psi^0_e > 0$) by the expressions

$$\psi^0_{**} = \psi^0_e + (\beta_2 - \beta_1)^{-1} \ln (i_{10}/i_{20}) \quad (35)$$

$$(\psi^0_{**})^{1/2} = (\psi_e{}^0)^{1/2} + (\beta_2 - \beta_1)^{-1} \gamma_2^{1/2} \delta^{-1} \ln (i_{10}/i_{20}) \quad (36)$$

If the full current i in the system is comparable to i_D the polarisation curves suffer a radical change of shape in the slow relaxation case. The method of calculation and some special cases are discussed in Ref.82.

The polarisation curves may be affected by field-induced phase transitions in the near-surface layer of the solid electrolyte (see Section III). This effect has been shown[89] to lead to a stepwise region ("jump") in the current–voltage characteristic of the system, the potential and the amplitude of the jump being determined by the parameters used above to define the thermodynamic and kinetic properties of the crystal.

The most important of the time-dependent solutions of the transport equations (in relation to studies of electrode processes and of the bulk properties of the system) are those describing the response of the system to small harmonic perturbations. In this case an approximate analytical solution of the system of non-linear equations in partial differentials can be obtained by changing to a system of ordinary linear equations: this change is justified if the amplitude of the harmonic signal is small enough. The method of investigating these systems by studying the relationship between a small harmonic signal and the voltage has been called the impedance method. The application of the impedance method to electrochemical systems is discussed in detail in Ref.90. Within the framework of this method the electrochemical cell is replaced by its corresponding equivalent circuit, in which each element relates to one particular process in the system. The choice of equivalent circuit is not unique, in general. Calculations of the impedance of solid electrolyte cells for different assumed models are described in several papers (see, for example, Refs.91–94).

IV. BASIS OF THE MICROSCOPIC APPROACH. PHYSICAL METHODS OF INVESTIGATION

In this Section we shall examine two groups of problems: 1) some aspects of the microscopic description of ionic transport processes in solid electrolytes, which have been developed in recent years, and 2) the theoretical foundations of the physical methods used experimentally both to justify the choice of microscopic models and to obtain numerical values of the characteristic parameters of the crystals.

The theory of microscopic processes in solid electrolytes is still far behind the stage of development of the theory of transport processes in normal solids. This explains the proliferation of different (and often incompatible) models proposed by various authors. Similarly, the physical methods so far applied to the study of microscopic processes in solid electrolytes have failed, on the whole, to make full use of their implicit possibilities, only a small proportion of the experimental techniques to solid-state physics having been brought to bear.

We shall therefore selectively aim our discussion at those concepts and methods whose value has already been convincingly demonstrated.

1. Microscopic Models of Transport Phenomena

Published theoretical treatments of transport phenomena in superionic crystals by the microscopic approach can be arbitrarily classified into a number of groups.

Many of the papers describe calculations of the diffusion coefficients and mobilities of point defects (interstitial ions or vacancies) under the influence of an externally applied potential. Some of the earlier models have relied on the quasi-free ion concept, analogous to the Sommerfeld–Drude–Lorentz approach to electronic transport phenomena in metals[95,96]. Armstrong and coworkers[97] applied the expressions of the theory of rate processes to a model of thermally activated translation jumps. In this type of calculation the conductivity is expressed, in accordance with experimental data, as $\sigma = \sigma_0 \exp(-E_a/T)$, where the physical significance of σ_0 and that of the activation energy E_a are different in different models. The E_a values for most of the "good" solid electrolytes are relatively small, and similar (~0.1 eV), but the range of σ_0 values extends over several orders of magnitude. Various explanations of this phenomenon have been proposed[98–103] (failure of the simple models when applied to the calculation of the frequency of "attempted jumps" between potential wells, failure to allow for cooperative motion, etc.).

Several papers have dealt with the microscopic calculation of the relationship between the diffusion coefficient and the mobility of the ions allowing for the correlation effects which cause deviations from the Nernst–Einstein relation[104–108].

In another group of papers the properties of the superionic crystal are calculated analytically from a model Hamiltonian[103,109–114]. Some of the earlier attempts[99,100] tried to describe the collective interactions of interstitial ions in superionic crystals by exactly the procedure applied to the electrons in an ordinary ionic crystal (the polaron model). This approach has the advantage of bringing to bear on the problem the well tried mathematical framework of polaron theory. The concept of small polarons was introduced to explain the Hall effect in solid electrolytes[115].

The lattice gas model[85,86,116] is similar to the approach used by Mahan[100]: it assumes the existence of particles described in the secondary quantisation formalism by anti-commutating generation and annihilation operators. The anti-commutation arises because a lattice site (or an interstitial) can be either empty or occupied by a single particle. The Hamiltonian for the sum over the lattice sites includes terms describing the interactions with nearest neighbours, jump terms, and in some treatments terms describing the interaction with phonons. This model has been used[85] in the one-dimensional form to calculate the transport heat Q of the ion, which defines the homogeneous part of the thermo-electric power (see Section III). At relatively low temperatures the parameter Q is found[85] to coincide with the activation energy for conduction E_a, as in the case of non-interacting particles; a three-dimensional treatment of the problem has also been given[86], with allowance for the interaction of the mobile ions with phonons. This interaction causes a small difference between the quantities Q and E_a ($Q < E_a$) due to the energy of formation of the polaron.

Yet another group of papers relies on computer calculations. In the early work of this type[117–119] the interionic interaction potentials were used to calculate the "potential contour" maps for the mobile ions in the crystal and hence

the activation energies, the crystallographic directions of highest ionic conductivity, etc. The energetics of both "shallow" and "deep" levels for ions, their numbers, and their relative position in space have been calculated for specific crystals[120]. This approach helps to determine, in particular, what proportion of the ions is involved in transport phenomena.

Lastly, some of the most recent publications on the theory of solid electrolytes have used the molecular dynamics method (a new method of studying systems of many particles[121]). The development of the molecular dynamics method was made possible by the availability of advanced computer techniques: the method is based on mathematical modelling of the motion of an ensemble of particles subjected to given interaction laws. Numerical solutions of the equations of motion yield the dynamic trajectories of the particles and hence, by applying the ergodic hypothesis, the mean values of the dynamic variables can be obtained. For example, an ensemble consisting of a large number of Ag^+ and I^- ions contained in a cube with periodic boundary conditions has been analysed in this way[122]. From the interaction potentials, whose parameters were chosen from the known ionic radii of Ag^+ and I^-, from the crystal structure of α-AgI, and from diffraction data, the motion of the Ag^+ ions was calculated directly. From results of this type the diffusion coefficient D of the Ag^+ ions (say) can be obtained directly, using the general definition

$$\lim_{t\to\infty}\langle r^2(t)\rangle = 6Dt + \text{const}\ ,$$

where $\langle r^2(t)\rangle$ is the mean-square displacement calculated by the molecular dynamics method#. Similar calculations give the correlation functions of the velocities (u) of the ions: $\langle u(t)u(0)\rangle$. The behaviour of these functions for different values of t characterises the frequency dependence of the conductivity $\sigma(\omega)$. Thus the parameters of the kinetic processes can be expressed through the initial micropotentials of the ionic interactions, which are obtained from independent data.

The molecular dynamics method has been used in studies of the properties of the following solid electrolytes: AgI,[123-127] CuI,[125] CaF_2,[127,128] $SrCl_2$,[129] and γ-Al_2O_3.[79] The characteristics of the superionic crystals which have been calculated include $\sigma(\omega)$, the distribution of the concentration of mobile ions, the diffusion coefficients, and the displacement of the ions in the rigid sublattice. In every case the agreement between calculation and experiment was good. The results also confirm the existence of phase transitions in many solid electrolytes.

2. Interaction with Electromagnetic Radiation

By virtue of its interaction with the individual particles and with the collective excitations present in the crystal, a beam of electromagnetic radiation passing through a solid electrolyte experiences both elastic and inelastic (i.e. accompanied by frequency changes) scattering processes. The inelastic scattering processes are most intimately connected with the microscopic characteristics of the crystal§.

#The result, $D = 2.5 \times 10^{-9}$ m^2 s^{-1}, is close to the value measured experimentally.

§These processes are also called Mandel'shtam–Raman–Brillouin scattering.

The intensity I_R of inelastically scattered radiation of frequency ω is given by the dissipative fluctuation theorem[130] as

$$I_R = A\varepsilon''/[1-\exp(-\hbar\omega/T)]\ , \qquad (37)$$

where $\varepsilon''(\omega)$ is the imaginary part of the complex dielectric constant $\varepsilon(\omega)$, and the quantity A is proportional to the square of the matrix element of the corresponding quantum-mechanical transition. The form of the denominator of Eqn.(37) stems from the fact that the quanta of electromagnetic radiation obey Bose–Einstein statistics.

The frequency-dependent conductivity $\sigma(\omega)$, which describes [like $\varepsilon''(\omega)$] the dissipative processes in the system, is related to ε'' by the expression

$$4\pi\sigma(\omega)/\omega = \varepsilon''(\omega)\ . \qquad (38)$$

If the frequency of the radiation is such that $\hbar\omega \ll T$, and the parameter A is weakly dependent on ω, it follows from (37) and (38) that $\sigma(\omega) \propto \omega^2 I_R$. The last expression shows that the inelastic scattering spectra contain direct information on the microscopic details of the conduction mechanism. Furthermore, independent determinations of the function $\varepsilon''(\omega)$, for example from infrared absorption and reflection data, can also be directly related to the frequency dependence of the conductivity $\sigma(\omega)$. Measurements of this type, using procedures which have become well established in solid-state physics (including dispersion expressions), have been applied to a large number of superionic crystals[131-161].

In one of the simplest models the function $\varepsilon(\omega)$ can be found by examining the frequency of a damped harmonic oscillator in an external electric field E:

$$\ddot{x} + \gamma\dot{x}\omega_0^2 x = zeE/m\ , \qquad (39)$$

where x, Ze, and m are the coordinate, the charge, and the mass (reduced) of the vibrating ion, ω_0 is the vibration frequency in the crystal lattice, and γ is the damping (dissipation) constant. Putting $E = E_0\exp(-i\omega t)$, where $i \equiv \sqrt{-1}$ is the imaginary unit, we can easily calculate from (39) the induced dipole moment $p = ezx$ and hence the polarisability $\alpha(\omega)$ of the system (since $p = \alpha E$). The function $\varepsilon(\omega)$ is then obtained by the formula $\varepsilon(\omega) = \varepsilon_\infty + 4\pi\alpha n$, where n is the number of vibrating ions which scatter radiation per unit volume, and ε_∞ is the value of $\varepsilon(\omega)$ in the limit of $\omega \to \infty$ (in an even more simplified model $\varepsilon_\infty = 1$). The resulting expression for $\varepsilon(\omega)$ is

$$\varepsilon(\omega) = \varepsilon_\infty + S\omega_0^2/(\omega_0^2 - \omega^2 - i\omega\gamma)\ , \qquad (40)$$

where S is a dimensionless constant [according to (39), $S = 4\pi z^2 \cdot e^2 n/m\omega_0^2$]. The function $\varepsilon''(\omega)$, according to Eqn.(40), is given by

$$\varepsilon''(\omega) = S\omega_0^2\omega\gamma/[(\omega_0^2-\omega^2)^2 + (\omega\gamma)^2]\ . \qquad (41)$$

The absorption spectra corresponding to Eqn.(41) should be characteristically bell-shaped (Lorentzian distribution). In spite of its simplicity, the starting model is found to be effective up to frequencies in the infrared region, and the inelastic scattering spectra of many solid electrolytes can be described satisfactorily by Eqns.(37) and (41).[131,133,135]

A direct generalisation of Eqn.(40), applicable to descriptions of the properties of ionic crystals in the infrared spectral region, can be written as

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_j \frac{S_j\omega_{0j}^2}{\omega_{0j}^2 - \omega^2 - i\omega\gamma}\ , \qquad (42)$$

where S_j is the dimensionless oscillator strength for mode j, which characterises the contribution of this mode to the static ($\omega = 0$) dielectric constant: $\sum_j S_j = \varepsilon_\infty - \varepsilon(0)$. The

absorption spectrum corresponding to Eqn.(42) is a set of peaks of the type described by Eqn.(41), usually overlapping.

The specific property of solid electrolytes is the presence of disorder in one of the crystal sublattices, which can manifest itself in a variety of effects associated with the interaction of radiation with matter: different ions, as a result of differences in their coordination, will have different vibration frequencies, and perturbations in the periodicity of the lattice will affect the selection rules, causing distortions in the optical spectra.

Temperature-induced phase transitions in solid electrolytes can also affect the probabilities of optical excitation of different frequencies. This effect is mathematically equivalent to a change in the parameter S_j, i.e. to a variation of the height of the corresponding peaks. If the symmetry of the crystal lattice is changed as a result of the phase transition, the selection rules for optical transitions will also be changed, causing individual peaks in the absorption spectrum to disappear (or appear). These effects have been very convincingly demonstrated experimentally[156,162,163].

Some attempts have been made to generalise the harmonic oscillator ensemble model in a slightly different direction by allowing for the specific features of the motion of ions in solid electrolytes. In particular, a model of an oscillator with a "finite memory" has been proposed[164]: according to this model the force acting on the ion at time t depends on the velocity $\dot{x}$ of the ion at some previous time. Mathematically this assumption involves replacing the term $\omega_0^2 x$ in Eqn.(39) by $\omega_0^2 \int_{-\infty}^{t} M(t-t')\dot{x}(t')dt'$, where $M(t-t')$ is the "memory function". If this function is chosen as

$$M(t-t') = \exp[-(t-t')/\tau_c],$$

where τ_c is the correlation time, in the case of a harmonic signal [$\propto\exp(-i\omega t)$] the above integral is directly calculable, and the final solution is obtained simply by replacing ω_0^2 by $\omega_0^2 i\omega/(i\omega - \tau_c^{-1})$ in Eqn.(40). In this case the conductivity is given by the expression

$$\sigma(\omega) = \frac{z^2e^2n}{m}\,\frac{\tau_c^{-1}(\omega_0^2 - \omega^2 + \gamma\tau_c^{-1}) + \omega^2(\tau_c^{-1} + \gamma)}{(\omega_0^2 - \omega^2 + \gamma\tau_c^{-1})^2 + \omega^2(\tau_c^{-1} + \gamma)^2}\,. \qquad (43)$$

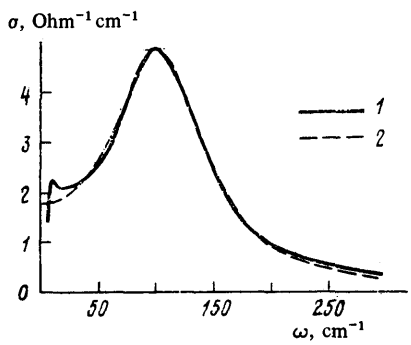


Figure 14. Frequency dependence of the conductivity [$\sigma(\omega)$] for α-AgI at 453 K:[164] *1*) experimental, *2*) calculated by formula (43).

The $\sigma(\omega)$ function calculated by Eqn.(43) for α-AgI with a suitable choice of parameters agrees very well with experiment for $\omega > 20$ cm^{-1} (see Fig.14).

The physical significance of the time τ_c is clear: for $\omega \ll \tau_c^{-1}$ the role of the electric field consists mainly in initiating the diffusional motion of the ion (the term proportional to ω_0^2 is small); conversely, for $\omega \gg \tau_c^{-1}$ the vibrational motion becomes predominant. According to Brüesch and coworkers[164] the characteristic τ_c^{-1} frequency of the transition between these two regimes is ~50 cm^{-1} (~1.5×10^{12} Hz). This value agrees well with that calculated by the formula $\tau_c^{-1} \cong (r_0^2/6D_1)^{-1}$, where r_0 is the distance between potential minima and D_1 is the diffusion coefficient of the interstitial ions.

The frequency dependence $\sigma(\omega)$ in α-AgI at relatively low frequencies ($\omega < 20$ cm^{-1})¶ has been explained[165,166] by allowing for the dependence of the motion of the ion in an alternating field upon the polarisation of the rigid sublattice, using a formalism similar to the above. A system of oppositely charged, interacting ions of two kinds has been discussed[166] by assuming that the ions of one kind can diffuse while those of the other kind are rigidly bound. The solution of the system of two equations obtained shows an apparent change in mass of the diffusion ions with frequency, since the polarisation of the medium (caused by interaction with other ions) either "succeeds" in following their motion or "fails" to do so[166]. Detailed microscopic studies of these phenomena are described in Ref.79.

Correlation effects resulting from the mutual interactions of the mobile ions are discussed in Refs.167–177.

3. Neutron Scattering

The neutron scattering method occupies a special place in the study of the properties of solid electrolytes, because the de Broglie wavelength of thermal neutrons is comparable to the interatomic distances found in typical crystals. At the same time (and unlike X-rays of the same wavelength) these neutrons have an energy comparable to the phonon energy of the crystal. Therefore, valuable information on the vibrational spectrum of the solid can be obtained by measuring the energy spectrum of the scattered neutrons.

Thermal neutrons are scattered by a crystal at a large number of lattice centres simultaneously, and therefore interference of the scattered waves is possible. The part of the scattered radiation affected by interference is called coherent scattering. In addition, different centres can scatter neutrons independently of each other, giving rise to incoherent scattering.

The scattering of neutrons by a system of many interacting particles is directly related to the behaviour of the space- and time-dependent pair correlation function $G(\mathbf{r}, t)$. The differential scattering cross-section within the solid angle $d\Omega$ and the energy range of scattered neutrons $d\mathscr{E} = \hbar d\omega$ can be expressed as

$$\frac{d^2\sigma}{d\Omega d\mathscr{E}} = \frac{a^2}{\hbar}\frac{k}{k_0}S(\varkappa, \omega)\,, \qquad (44)$$

where $S(\kappa, \omega)$ is the Fourier transform of the correlation function $G(\mathbf{r}, t)$ (the dynamic structure factor), $\kappa = \mathbf{k} - \mathbf{k}_0$ (where $\mathbf{k}_0$ and $\mathbf{k}$ are the wave vectors of the incident and of the scattered neutron), the frequencies ω are expressed in terms of the energy changes $\hbar\omega = \hbar^2(k_0^2 - k^2)/2m$ (where m is the mass of the electron), and a is the scattering length.

¶However, we should note that according to Gebhardt and coworkers[154] the conductivity of α-AgI at frequencies between 8×10^9 and 4×10^{10} Hz is described by a simple expression of the Drude type.

Inelastic coherent scattering processes are the most interesting in studies of the dynamic properties of a crystal lattice. Scattering is assumed to take place on nuclei located at lattice sites with a time-dependent displacement determined by the lattice vibrations. The correlation function (for single-phonon scattering) allows for the energy and momentum conservation laws:

$$\hbar^2(k^2-k_0^2)/2m=\hbar\omega_j(\mathbf{q}); \quad \mathbf{k}-\mathbf{k}_0=2\pi\mathbf{b}+\mathbf{q}\,, \qquad (45)$$

where q is the wave vector of the phonon, b is the reciprocal lattice vector, and $\omega_j(\mathbf{q})$ is the frequency of the j-th branch of the normal vibration to which the phonon is assigned. By measuring the one-phonon scattering cross-section of the neutrons we can determine the dispersion laws $\omega = \omega_j(\mathbf{q})$ which characterise the phonon spectrum of the crystal.

Phonon spectra have been obtained experimentally for the following series of solid electrolytes: AgI,[178-181] Ag_3SI and Ag_3SBr,[182] $RbAg_4I_5$,[180,181] BaF_2,[183-185] $SrCl_2$,[183-185] PbF_2,[185,186] Li_2SO_4,[187] $LiAlSiO_4$,[188] and β-Al_2O_3.[189,190] Special attention was paid to the spectral changes accompanying the transition of the superionic crystals into the disordered phase[178,179,182,191]. A study of the dispersion curves of silver iodide at different temperatures[178,191] revealed the loss of one low-energy optical mode during the $\beta \to \alpha$ structural phase transition. This is explained[178] by assuming that a relatively small amount of energy is expended in the rearrangement of the rigid (iodide) anion sublattice attending the transition to the superionic state. Similar results were obtained for the superionic conductors Ag_3SI and Ag_3SBr.[182]

Neutron scattering has been used also to study the behaviour of ions in disordered phases of superionic crystals. A study[96,181] of the quasi-elastic scattering of cold neutrons in the α-phase of AgI may be taken as an example. The experimental results were interpreted on the assumption that scattering occurs exclusively on the silver cations†. The following microscopic model was adopted[96] to calculate the correlation function. The ions take part in two independent types of motion: translational, and local. The translational motion of the ion is described by the hopping mechanism: the particle resides in a fixed position for a time τ_0, after which it jumps (in a time τ_1') to a point a distance l_0 away. The local motion of the ion is treated as the random ("Brownian") motion of particles in some limited regions ("cavities") of the crystal, defined by the geometry of the iodine sublattice.

The best agreement between calculated and experimental curves is obtained for the following values of the parameters: $\tau_0 = 7.5 \times 10^{-12}$ s, $\tau_1' = 16.5 \times 10^{-12}$ s, $l_0 = 5$ Å. The diffusion coefficient of the silver cations D can be calculated by the formula $D = l_0^2/6(\tau_0 + \tau_1')$. Inserting the above values of the parameters we find $D \cong 1.75 \times 10^{-9}$ m^2 s^{-1}, in good agreement with the experimental value $D_{exper} \cong 2 \times 10^{-9}$ m^2 s^{-1}. Detailed studies of the quasi-elastic neutron scattering spectra of α-AgI single crystals[181] have revealed a strong anisotropy in the motion of the Ag^+ ions#.

†The scattering cross-section of iodine is much smaller than that of silver.

#According to Cava and coworkers[192] the average jump length of the cations is $l = 1.79$ Å, but this value is inconsistent with the present result. This problem is examined specifically in Ref. 193.

To conclude this Section we note that the crystal structure of disordered phases in superionic crystals has been studied not only by the quasi-elastic scattering of neutrons, but also by diffuse neutron and X-ray scattering (X-ray and neutron diffraction).[192-211] For example, neutron diffraction experiments with α-Ag_2S have shown[197] that the silver cations are not localised in fixed positions, but behave as a "lattice liquid". The inelastic neutron scattering spectra of $RbAg_4I_5$ are interpreted[103] in terms of a model of the Brownian motion of the diffusing Ag^+ ions in a sinusoidal potential field.

4. Magnetic Resonance

Under NMR conditions, which are highly relevant in studies of superionic crystals[212,213], the system of nuclear spins interacts with an external magnetic field H_0; furthermore, the spins also interact among themselves and with the "lattice".

Let us examine the behaviour of the integral magnetic moment M of a large number of spins (magnetic moments) at a temperature T. Let the external field H_0 be directed along the z axis. In general, the component M_z of the vector M may differ from its equilibrium value M_0, corresponding to a constant field H_0, owing to the fluctuations of the local magnetic field within the crystal. Under these conditions the approach to equilibrium as a result of the interaction of the system of spins with the crystal lattice (in particular, with the phonons) obeys the phenomenological expression (Bloch equation) [214]

$$dM_z/dt=-(M_z-M_0)/T_1\,, \qquad (46)$$

where T_1 has been called the spin–lattice relaxation time.

In discussions of relaxation processes in solid electrolytes the local magnetic field is usually assumed to be produced by the fluctuating magnetic fields of the mobile ions. The time characteristics of the local fields are described in general by the time-dependent pair correlation function $G(t)$, which usually decreases exponentially by the law $\exp(-t/\tau_1)$, where τ_1 is the "relaxation" time of the correlation. Since the nature of the fluctuations changes with temperature, the quantity τ_1 is a function of temperature, and can be expressed as $\tau_1 = \tau_{10}\exp(E_a^*/T)$, where E_a^* is an activation energy and the constant τ_{10} is formally defined as the value of τ_1 at $T \to \infty$.

The relaxation time T_1 is related to τ_1 by the expression[214]

$$\frac{1}{T_1} = B\frac{\tau_1}{1+\omega_0^2\tau_1^2}\,, \qquad (47)$$

where $\omega_0 \equiv \gamma g H_0$ is the precession frequency of the spin in the magnetic field H_0 (the Larmor frequency) and B is a quantity independent of ω_0 and τ_1 and proportional to the intensity of the local magnetic field.

The temperature dependence of the spin–lattice relaxation time T_1 has been studied experimentally at both low and relatively high temperatures in a series of solid electrolytes[215-224]. The activation energies E_a^* obtained from these data by Eqn. (47) for the low-temperature phases of some superionic crystals are satisfactorily consistent with the E_a values calculated from the temperature dependence of the ionic conductivity:

Crystal	PbF_2	$LiAlSiO_4$	CuI
E_a^*, eV	0.7 [217]	0.8 [215]	0.5 [218]
E_a, eV	0.7 [225]	0.7 [226]	0.6 [227]

This agreement between the two sets of activation energy is not surprising, since the transport processes in the low-temperature region occur by jumps of individual ions

between different positions in the crystal. Under these conditions the time τ_1 can be identified with the time between jumps. This agreement is a powerful argument in favour of the validity of the postulates on which these models are based.

Measurements at relatively higher temperatures in the disordered phase (superionic state) have shown that the relaxation rate T_1^{-1} decreases exponentially as the temperature increases[98,219,221]. For $\omega_0\tau_1 \ll 1$, and assuming that the local field (and therefore also the parameter B) is proportional to the concentration of mobile particles $n(T)$, we obtain from (47)

$$T_1^{-1} \propto n(T)\tau_1(T)\,. \qquad (48)$$

In the light of Eqn.(48) the experimental results are readily explained by noting that the quantity $n(T)$ is only weakly dependent on temperature, as discussed in Section II. Thus, the qualitative statements on the "molten" state of one of the sublattices in solid electrolytes[217,218] are experimentally confirmed.

The NMR method has been used in structural studies of superionic conductors, since the local symmetry and the coordination of ions taking part in the transport process can be determined from the NMR spectra of nuclei with a quadrupole moment[228-233]. The method has been found convenient also in studies of phase transitions, especially in $RbAg_4I_5$ [234] and in $Li_{14}Zn(GeO_4)_4$.[235]

However, some results of NMR studies on solid electrolytes are not easily interpreted within the model of independent motion of ions[215,219-221]. These observations suggest the need for many-particle concepts (in particular, allowance for ion correlations) in the description of the transport properties of superionic crystals.

The effect of disorder in one sublattice on the ESR spectra has been demonstrated in solid electrolytes containing paramagnetic ions[236-238]. The ESR method has been used also to study the distribution of impurity ions in superionic crystals[239-243].

* * *

Our analysis of theoretical and experimental results has shown that considerable progress has been made in recent years in understanding the physical basis of the phenomena in solid electrolytes, though many important and interesting problems still await a solution. The set of problems associated with the superionic conduction phenomenon has now been clearly formulated as a self-contained and quite extensive scientific discipline.

The thermodynamics of superionic conduction are closely associated with those of other solid-state phenomena which have been more fully investigated (disorder in alloys, in solid solutions, and in ferroelectrics). We should stress that some of the theoretical results discussed in this review (in particular, the possible existence of bitransitions, and the stimulation of polymorphic transformations in crystalline structures by the presence of disorder in one of the sublattices) are directly relevant to a much wider range of materials.

The discontinuous change in ionic conductivity induced by an external electric field may be found to have practical as well as purely scientific interest.

Ionic transport phenomena in solid electrolytes have a number of specific features whose study offers a better understanding of the analogous phenomena in liquid electrolytes on the one hand and in "normal" ionic crystals on the other hand. We can expect the present intensive studies of the structural, thermodynamic, and kinetic properties of solid electrolytes to lead to a far more detailed knowledge of the behaviour of these materials.

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Catalytic Cyclo-oligomerisation Reactions of Lower Olefins and Alkanes with Formation of Aromatic Hydrocarbons

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The results of studies devoted to the aromatisation of lower (C_2-C_5) olefins and alkanes in the presence of a number of metal oxide and oxide catalysts are examined. The type of aromatisation discussed constitutes a new potential source of benzene and its nearest homologues, the need for which has been rapidly increasing.
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I. INTRODUCTION

The requirement for benzene and its derivatives is at present very great[1-3]. According to Fick[2], the consumption of benzene in the USA will exceed by 1985 the total 1965 requirement by a factor of two for the manufacture of ethylbenzene alone. The overall consumption in 1985 will double compared with the 1976 level, which corresponds to an average annual increment of 7.5%. The great practical value of theoretical and technical developments directed towards the creation of novel processes and the discovery of new possibilities for the synthesis of valuable aromatic hydrocarbons is therefore evident. The important problem of expanding the raw materials base for the manufacture of aromatic hydrocarbons is related to these tasks.

New possibilities for synthesising aromatic hydrocarbons by the dehydrocyclo-oligomerisation of C_2–C_5 light olefins and alkanes[4-15], and in a number of subsequent communications, are of undoubted interest. A characteristic of the cyclo-oligomerisation of C_2–C_3 hydrocarbons is that their aromatisation results in the preferential formation of benzene and toluene[7,11]. It is known that benzene is the primary starting material among aromatic hydrocarbons for industrial organic synthesis and is used to synthesis styrene, cyclohexane, caprolactam, phenol, maleic anhydride, and intermediates for the manufacture of detergents and dyes. Toluene is the starting material for the manufacture of benzene, phenol, benzyl chloride, and various types of varnishes, dyes, and resins.

The synthesis of aromatic hydrocarbons by the dehydrocyclo-oligomerisation of lower olefins and alkanes can be arbitrarily divided into two groups of reactions—non-oxidative and oxidative. The first group includes the conversion of lower (mainly C_2–C_4) olefins into benzene and other aromatic hydrocarbons in the presence of metal-containing and certain oxide catalysts. These reactions have been discussed in the literature under similar names—dehydrocyclo-oligomerisation, cyclodimerisation, cyclotrimerisation, and also aromatisation of lower olefins and alkanes. A distinctive feature of the above group of reactions is that they occur without the supply of gaseous oxygen to the reaction zone and without the participation of oxygen which forms part of the oxide catalyst. In the present review these reactions of lower olefins and alkanes will be referred to as non-oxidative cyclo-oligomerisation. The second groups of reactions includes different versions of the oxidative aromatisation of lower hydrocarbons, which occurs in the presence of various oxide catalysts at 500–600 °C.

The present state of studies on the cyclo-oligomerisation of olefins and the dehydrocyclisation of lower alkanes with formation of benzene and its homologues, mainly in the presence of metal oxides and a number of oxide catalysts, in the non-oxidative and oxidative versions of the reaction is briefly assessed below.

II. DEHYDROCYCLODIMERISATION OF C_3–C_5 OLEFINS AND ALKANES IN THE PRESENCE OF VARIOUS METAL-CONTAINING AND CERTAIN OXIDE CATALYSTS

The first data on the dehydrocyclo-oligomerisation of lower C_3–C_4 olefins with formation of aromatic hydrocarbons were published by Soviet workers[4,5,16-19].

It has been shown[4] that n-butene gives rise to olefins in the presence of an aluminosilicate catalyst at 370 °C; following an increase of temperature to 450–500 °C, aromatic hydrocarbons (benzene, xylenes, and trimethylbenzenes) are formed together with olefins. The polymerisation of isobutene in the presence of an alumina–molybdenum oxide catalyst has been investigated[5] and isomeric xylenes have been detected in the reaction products (400 °C) and isolated. It has been shown[16,17] that aromatic hydrocarbons can be the main products of the conversion of propene over zinc chloride. The polymerisation and aromatisation of propene in the presence of molybdenum/alumina and platinum/alumina catalysts has also been studied[18,19].

The aromatisation of lower C_3–C_5 alkanes in the presence of a number of metal oxides and oxide catalysts was first described by Csicsery in a series of papers[6-10] published in 1969–1970. The dehydrocyclodimerisation of lower alkanes has been studied most thoroughly in relation to butane (and butenes) on platinum/alumina and certain oxide catalysts[6,8,9].

The dehydrocyclodimerisation of propane and propene in the presence of platinum/alumina catalysts, alumina, and mixed oxide catalysts containing bismuth, tin, and nickel oxides as well as a number of others has been studied by Usov and coworkers[20-25].

The dehydrocyclodimerisation of lower C_3–C_5 alkanes takes place at relatively high temperatures. As a rule, the reaction takes place above 430–450 °C. Thus the equilibrium

constants of the reaction 2isobutane ⇌ p-xylene + $5H_2$ at 427° and 527 °C are respectively 16.23 and 1.22×10^4.[6] The reaction takes place successfully in the presence of bifunctional catalysts with the optimum combination of dehydrogenating and acid properties, i.e. having a fairly high dehydrogenating activity and active in acid–base reactions.

A large series of metal oxide and oxide dehydrocyclodimerisation catalysts have been tested[6–10]. Among oxide catalysts, vanadium and chromium oxides are the most active in the reaction discussed; among metals, platinum has proved most successful. The usual overall content of the dehydrogenating component is 0.6–3.0% (for metal oxide catalysts) and 0.3–35% (for complex oxide catalysts) relative to the mass of the carrier. Alumina has been used successfully as the carrier, particularly alumina promoted with a halogen. In addition, amorphous and crystalline aluminosilicates, magnesium oxide, and silicon–magnesium oxides have been used as carriers for catalysts of the dehydrocyclisation of lower alkanes.

The platinum/alumina catalyst proved to be the best of the metal oxide catalysts of the dehydrocyclodimerisation of lower alkanes investigated by Csicsery[6]. Fig.1 shows how the platinum content in the platinum/alumina catalyst affects the degree of conversion of isobutane into aromatic hydrocarbons and the yield of the latter in the dehydrocyclodimerisation reaction. It follows from the results that the active surface of platinum in the catalyst employed (0.5–2.5% Pt/Al_2O_3) is approximately proportional to the platinum content in the catalyst. With increase of the platinum content, the yield of aromatic hydrocarbons falls as a consequence of the considerable intensification of the cracking and coke forming reactions. The author[6] therefore concluded that, under the conditions investigated (the carrier, temperature, space velocity, etc. employed), the optimum concentration of platinum in the catalyst is ~0.8 wt.% or a little less.

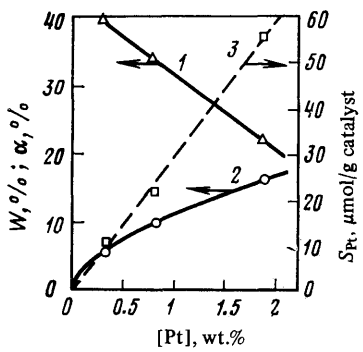


Figure 1. The influence of the concentration of platinum in the Pt/Al_2O_3 catalyst on the dehydrocyclodimerisation of isobutane to aromatic hydrocarbons (560 °C): 1) the yield of aromatic hydrocarbons W; 2) the degree of conversion α of iso-C_4H_{10}; 3) the adsorption capacity of the catalyst[6].

In the presence of this catalyst at 560 °C, C_3–C_5 alkanes undergo a whole series of reactions[6,7]: cracking with formation of methane and other hydrocarbons having a lower molecular weight than the initial compound; dehydrogenation; dehydrocyclodimerisation with formation of aromatic hydrocarbons; coke formation. The yield of aromatic hydrocarbons increases in the sequence propane < butane < pentane and is 9–15, 18–22, and 34–37 wt.% respectively. The main aromatic hydrocarbon obtained as a result of the dehydrocyclodimerisation of propane is benzene[7] the main aromatic compounds obtained as a result of the transformation of butanes are xylenes and toluene; benzene and C_9–C_{10} aromatic hydrocarbons have been detected in much smaller amounts[6]. Pentane gives rise to appreciable amounts of toluene and benzene and also to hydrocarbons with higher molecular weights such as naphthalene, indene, and other condensed compounds[7].

The dependence of the composition of the products of the reaction of isobutane on its contact time with 0.8% Pt/Al_2O_3 has been studied[6]. It follows from Fig.2 that, with increase of contact time, there is a sharp acceleration of the dehydrogenation process accompanied by the formation of butenes, whose amount passes through a definite maximum. The concentration of aromatic compounds in the reaction products increases more gradually. The yield of coke and cracking products increases approximately linearly with increasing contact time. Analysis of the shape of the curves describing the increase of the content of butenes and aromatic compounds led the author[6] to the conclusion that the dehydrocyclodimerisation of isobutane is a consecutive reaction on the assumption that butenes are intermediates in the formation of aromatic hydrocarbons. Rapid skeletal isomerisation was also noted. For longer contact times, the ratio isobutenes: :n-butene approaches the equilibrium value (0.73 at 560 °C). Special experiments showed[6] that the xylenes and ethylbenzene, formed as a result of the dehydrocyclodimerisation of isobutane, undero dealkylation with increase of contact time and are converted into toluene and benzene.

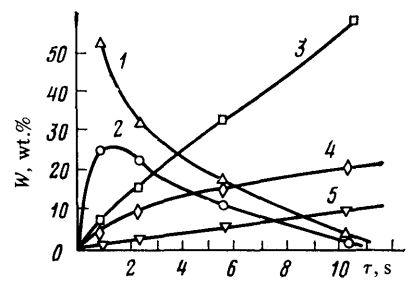


Figure 2. The influence of contact time on the composition of the isobutane dehydrocyclodimerisation products at 560 °C in the presence of 0.8% Pt/Al_2O_3: 1) C_4H_{10}; 2) the sum of C_4H_8 hydrocarbons; 3) the overall yield of C_1 and C_2 hydrocarbons; 4) the sum of aromatic hydrocarbons; 5) coke[6].

An important factor influencing the degree of dehydrocyclodimerisation of lower alkanes and the composition of the aromatic component of the catalytic reaction mixture is the acidity of the catalyst. The latter depends on many factors, including the nature and method of preparation of the carrier, the composition of the compound containing the active component, the method of its deposition, the presence of acid or alkaline additives, etc. Some of these parameters have been varied[6]. An increase of acidity tends to increase the yield of aromatic hydrocarbons.

In the presence of strongly acid catalysts isobutane and n-butane give rise to reaction products with a very similar composition of aromatic hydrocarbons. The latter is apparently due to the fact that the more acid catalyst promotes

the greatest approach of the composition of the initial mixture of isobutenes and n-butenes to the equilibrium composition under the reaction conditions. A definite dependence of the activity of the catalyst in the dehydrocyclodimerisation of isobutane on the acidity of the catalyst has been observed[6], a change in acidity being reflected in the isobutenes:n-butenes ratio in the reaction mixture. Furthermore, in the presence of weakly acid catalyst, n-butane gives rise mainly to ethylbenzene and styrene, while isobutane forms *p*-xylene. At the same time, in the presence of strongly acid catalysts both C_4 alkanes give rise to products with the same composition of the aromatic hydrocarbons.

Interesting data have been published[6] on the reactions of isobutane under dehydrocyclodimerisation conditions over three catalysts: Pt/Al_2O_3; $Pt/Al_2O_3 + Al_2O_3$; $Pt/Al_2O_3 + Al_2O_3 - SiO_2$. In the case of the last two catalysts, used in the form of a mechanical mixture of 0.8% Pt/Al_2O_3 and the "acid component", an appreciable (by a factor of ~2) increase of the yield of aromatic hydrocarbons and a clear decrease of the amount of the products of dehydrogenation of butenes and butadienes were observed.

Csicsery[9] put forward and tested the hypothesis that there is a definite relation between the acidity of the catalyst and its oligomerising activity. It was assumed that olefins are dimerised mainly on acid surface centres. To test this hypothesis, *trans*-but-2-ene was passed over various acid catalysts without a metal. In the presence of alumina and aluminosilicate the butene readily isomerised to a mixture of *cis*-but-2-ene and but-1-ene. A proportion of the butenes were converted into liquid products consisting of linear and cyclic oligomers and also of aromatic hydrocarbons. The concentration of the latter in the catalytic reaction mixtures was appreciably lower than in the presence of corresponding platinum-containing catalysts—Pt/Al_2O_3, and $Pt/Al_2O_3-SiO_2$.

Consequently catalysts not containing the hydrogenating–dehydrogenating component successfully initiate the aromatisation reactions of linear dimers, the disproportionation of polyalkylbenzenes, cracking reactions, etc. but nevertheless to an appreciably small extent than the corresponding metal-containing catalyst. The important role of the acidity of the catalyst has been demonstrated in the study of the reactions of *trans*-but-2-ene over aluminosilicate to which various alkali metals have been added. With increase of the concentration of sodium in the catalyst, the rates of dehydrocyclodimerisation, skeletal isomerisation of olefins, cracking, and coke formation appreciably decreases.

The degree of dehydrocyclodimerisation of butane decreases significantly when the initial hydrocarbon is diluted with hydrogen. It is apparently due to the appreciable acceleration of the hydrogenolysis; in the presence of Pt/Al_2O_3 at 560 °C up to 85% of the butene was converted into methane during the first 10 minutes of the experiment and the main bulk of the aromatic hydrocarbons were demethylated to benzene[6]. In the absence of hydrogen, an increase of the hydrocarbon pressure in the system in the range from 1 to 50 atm entailed an increase of the rate of dehydrocyclodimerisation of the alkane and to a lesser extent an increase of the rate of cracking. Since the dehydrocyclodimerisation of alkanes led to the evolution of a large amount of hydrogen (5 moles of H_2 for 2 moles of the alkane), it is recommended that the initial alkane be diluted with an inert gas.

The question of regeneration of the catalysts of the dehydrocyclo-oligomerisation of lower hydrocarbons has so far been inadequately elucidated. The relatively extensive coke formation on these catalysts necessitates regular and frequent regenerations. Compared with platinum catalysts, the oxide catalysts containing variable-valence elements are much more stable under the conditions of frequent regeneration. It is therefore useful to employ catalysts containing Group V–VII transition metal oxides, which can be usually repeatedly regenerated without significant loss of activity. Vanadium, molybdenum, chromium, tungsten, and manganese oxides deposited on alumina have been investigated[8]; the highest conversion of n-butane was observed in the presence of the first two oxides.

The influence of temperature on the degree of dehydrocyclodimerisation of n-butane in the presence of chromium oxide/alumina catalyst prepared by the method of Pines and Haag[26] has been studied[8], the experiments being performed in the range 490–593 °C. The highest yield of aromatic hydrocarbons was reached at 593 °C. With increase of temperature, an increase of the yields of methane, ethane, ethylene, and coke was noted. The maximum yield of aromatic hydrocarbons, evaluated taking into account the recirculation of the C_3-C_5 hydrocarbons, was observed at 250 °C.

As in the presence of metal-containing catalysts, the acidity of the carrier plays the major role in the case of oxide catalysts. A series of chromium oxide–potassium oxide/alumina catalysts (0.1 wt.% K) with different acid carriers have been studied in relation to the dehydrocyclodimerisation of n-butane[8]. The yield of aromatic hydrocarbons is higher in the presence of catalysts containing η-Al_2O_3 or fluorinated Al_2O_3 (on the latter, the yield of coke is minimal).

The dehydrocyclodimerisation of propane and isobutane on an industrial platinum/alumina catalyst and also the dehydrocyclodimerisation of propene in the presence of alumina specimens of different acidity have been studied in detail[20–25]. The behaviour of propane, propene, and isobutane in the presence of the platinum/alumina catalyst[21,22] and of propene and C_6 hydrocarbons on alumina[23,24], as well as the influence of pyridine and ammonia on the dehydrocyclodimerisation of propane and propene[21,23] have been investigated; finally, alumina specimens of different acidity have been studied by spectroscopic methods[23]. The results enabled the authors to put forward a series of well-founded hypotheses concerning the mechanism of the dehydrocyclodimerisation of propane in the presence of the platinum/alumina catalyst. In particular, it has been shown that, under pulsed conditions in the presence of an industrial platinum/alumina catalyst in the temperature range 560–620 °C, propane undergoes far-reaching transformations in cracking, dehydrogenation, and aromatisation reactions. Depending on the experimental conditions, the yield of aromatic hydrocarbons then amounts to between 0.4 and 17% relative to the propane passed through the system.

The results enabled the authors[21,22] to suggest that propene is an intermediate in the dehydrocyclodimerisation of propane to aromatic hydrocarbons. A similar behaviour has been noted in the reactions of isobutane. The role of olefins in the aromatisation of lower alkanes has been studied in greater detail in relation to the reactions of propene. It was found that in the presence of platinum/alumina catalysts, propene undergoes more far-reaching transformations than propane, particularly with formation of aromatic hydrocarbons.

The same workers[25] described catalytic reactions of the propane–butane fraction of the gas associated with petroleum in the presence of the platinum/alumina catalyst. The transformation of the propane–butane fraction is a complex process consisting of a series of consecutive-parallel reactions, the principal of which are dehydrogenation and cracking of propane and butanes. The olefins formed in the dehydrogenation process subsequently undergo oligomerisation with formation of C_6 and C_8 dimers. The formation of aromatic C_8 and C_9 hydrocarbons, in the first place benzene and toluene, takes place as a result of the C_6-dehydrocyclisation of linear oligomers with the corresponding composition and structure. At the same time benzene (and toluene) are formed as a

result of the demethylation of homologues with a higher molecular weight, as shown by the increase of the concentration of aromatic C_6–C_9 hydrocarbons with increase of temperature and contact time.

In order to elucidate the role of the carrier in the bifunctional platinum/alumina catalyst in the dehydrocyclodimerisation of propane, a study has been made[23,24] of the reactions of propene in the presence of halogenated and alumina not promoted with a halogen. Starting from 250 °C and up to 475 °C, propene dimerises and the concentration of C_6 olefins increases from 3.6 to 16.8%. In the range 520–620 °C propene undergoes far-reaching transformations on fluorinated alumina, the principal reaction being aromatisation.

With increase of the acidity of the catalyst in the sequence γ-Al_2O_3 < γ-Al_2O_3(Cl) < γ-Al_2O_3(F), the overall degree of conversion of propene increases and the yield of aromatic hydrocarbons also rises. In the presence of γ-Al_3O_3(F) isobutene undergoes far-reaching transformations under similar conditions, mainly with formation of aromatic C_8 hydrocarbons.

It has been shown by the pulsed poisoning of fluorinated alumina with ammonia or pyridine that both bases suppress the aromatisation of both propene and C_6 hydrocarbons. It was therefore postulated[23,24] that the dimerising, dehydrocyclising, and dehydrogenating functions of alumina are associated with its acidity. It has been suggested that the first, slowest stage of the conversion of propene is its dimerisation, which can take place on protic acid centres of the catalyst via the carbonium ion mechanism or with participation of Lewis centres via a radical mechanism. The subsequent reactions of the dimers are apparently much faster and involve the formation of five- and six-membered cyclo-olefins and aromatic hydrocarbons and also cracking.

The aromatisation of lower olefins over alumina, aluminosilicates, and activated carbon has been studied[27,28]. The results confirmed that the aromatisation of lower olefinic hydrocarbons is a complex process leading to the formation not only of aromatic hydrocarbons but also of gaseous and liquid aliphatic products and naphthenes. With increase of the number of carbon atoms in the olefin molecule, the degree of conversion of the initial hydrocarbon also increases and the content of aromatic hydrocarbons in the liquid catalytic reaction mixture rises.

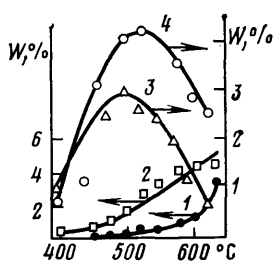


Figure 3. The influence of temperature on the yield of aromatic hydrocarbons W in the aromatisation of C_3H_6 in the presence of Al_2O_3.F: 1) C_6H_6; 2) $C_6H_5CH_3$; 3) aromatic C_9–C_{11} hydrocarbons; 4) xylenes[28].

The data obtained in the presence of fluorinated alumina are presented in Figs.3 and 4. It follows from the results that an increase of the temperature of the dehydrocyclodimerisation of propene and isobutene in the presence of alumina from 300° to 625 °C is accompanied by an increase of the degree of conversion of the initial olefins; aromatic hydrocarbons are formed appreciably only above 500 °C. The greatest selectivity in relation to aromatic hydrocarbons is reached at 550–625 °C. The increase of contact time is accompanied by an appreciable increase of the degree of conversion of the initial olefins but does not have an appreciable effect on the composition of the liquid reaction products and the selectivity of the reaction in relation to aromatisation.

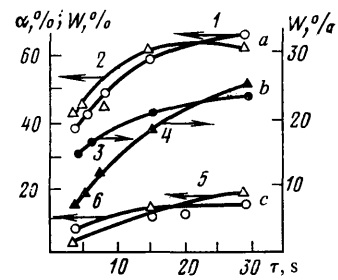


Figure 4. The influence of contact time on the aromatisation of C_3H_6 in the presence of Al_2O_3.F: *a*) the degree of conversion α of C_3H_6; *b*) the yield of aromatic hydrocarbons W relative to C_3H_6 which has reacted; *c*) the yield relative to the C_3H_6 passed through the system; 1), 3), and 5) 600 °C; 2), 4), and 6) 550 °C.[28]

It was noted above that in his study of the dehydrocyclodimerisation of butanes, Csicsery[6] suggested that the given reaction has a consecutive mechanism. In order to elucidate the role of olefins in the dehydrocyclodimerisation of alkanes, a study was therefore made[9] of the conversion of but-2-ene in the presence of the platinum/alumina catalyst. The higher degree of conversion of butene into aromatic hydrocarbons than for butane under similar conditions was established. The but-2-ene conversion products for short contact times proved to be mainly C_6–C_8 olefins and naphthenes. For longer contact times, a relatively larger amount of aromatic hydrocarbons and a much smaller amount of naphthenes were found in the reaction products. This change in the composition of the catalytic reaction mixture shows, according to the author[9], that the dehydrocyclodimerisation of butenes does indeed proceed via the initial formation of C_6–C_8 olefins and naphthenes.

In his treatment of the mechanism of the dehydrocyclodimerisation of butanes in the presence of bi- and polyfunctional catalysts, Csicsery[10] discusses a consecutive scheme consisting of the following stages: (1) dehydrogenation of alkanes to mono- and di-olefins; (2) dimerisation of olefins on acid centres; (3) aromatisation of unsaturated dimers; (4) isomerisation, transalkylation, and dealkylation of the aromatic hydrocarbons obtained initially with formation of a large number of C_8–C_{10} alkyl- and dialkyl-benzenes.

In order to refine the details of the first stage—the formation of olefinic and diolefinic hydrocarbons—experiments with butenes were carried out[9]. The rate of aromatisation of the latter proved to be 2–2.5 times higher than that of butane; the butene ⇌ butadiene equilibrium is established very rapidly; the cracking of butenes is slower and the rate of coke formation is appreciably higher than for butane. It has

been suggested that olefinic and diolefinic hydrocarbons are formed on dehydrogenating catalyst centres:

$$C_4H_{10} \xrightarrow{-H_2} C_4H_8 \xrightarrow{-H_2} C_4H_6 .$$

The second stage—catalytic dimerisation of unsaturated hydrocarbons—occurs mainly on the surface of acid centres on the carrier.

The mode of the third stage—aromatisation of dimerised olefins and diolefins—depends primarily on the experimental conditions and the catalyst. An increase of temperature accelerates the aromatisation of dimers and at the same time favours dealkylation. The latter is apparently responsible for the increase of the yield of benzene and toluene relative to C_9–C_{10} aromatic hydrocarbons. An increase of contact time leads to an increase of the yield of aromatic hydrocarbons compared with naphthenes. Under these conditions, an increase of contact time increases, like the increase of temperature, the contribution of the dealkylation reaction with formation of benzene and toluene. The dimers are aromatised much faster on the dehydrogenating catalyst centres than on the acid centres. However, the latter are also necessary, because, according to the author[9], five-membered naphthenes isomerise to six-membered naphthenes on such centres.

The fourth stage—isomerisation, transalkylation, and dealkylation of primary aromatic hydrocarbons—is accelerated, as noted above, by an increase of the reaction temperature, an increase of contact time, and finally by the acid catalyst centres. As a result of the reactions enumerated above, the n-butane catalytic reaction mixture contains the majority of the possible C_6–C_{10} aromatic hydrocarbons.

With increase of temperature, the cracking and coke forming reactions are accelerated simultaneously. The composition of the butene conversion products suggested[9] that C_3 and C_5 hydrocarbons are formed via the mechanism

$$2C_4H_8 \rightarrow C_8H_{16} \rightarrow C_5H_{10} + C_3H_6 .$$

Above 500 °C, direct cracking of butenes takes place with an appreciable yield:

$$C_4 \rightarrow CH_4 + C_3 \quad \text{or} \quad C_4 \rightarrow 2C_2 .$$

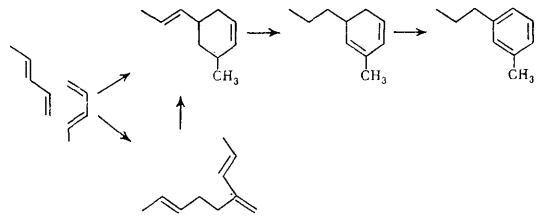
As a result, the following general mechanism has been suggested[10] for the conversion of butanes into aromatic hydrocarbons:

$$\begin{array}{ccccc} C_4H_{10} & \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} & C_4H_8 & \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} & C_8H_{16} \xrightarrow{k_3} C_6H_4(CH_3)_2 \\ \downarrow k_4 & & & & \downarrow k_5 \\ C_3 + CH_4 & & & & C_3 + C_5 \end{array} .$$

Depending on the rate constant ratios for the above reactions, one or other pathway predominates. It follows from the results that the best catalyst of the dehydrocyclodimerisation of alkanes should have the following properties[10]: (a) it should accelerate the dehydrogenation of alkanes more than the dimerisation of olefins on the acid component ($k_1 > k_2$); (b) it should lead to the aromatisation of the dimers on the dehydrogenating component being much faster than cracking and faster than the dimerisation of the acid component: $k_5 \ll k_3 \gg k_{-2}$; $k_3 > k_2$. The formation of dimers and trimers has also been noted[7] in the dehydrocyclodimerisation of n-pentane. The curve relating the yield of aromatic hydrocarbons to the number of carbon atoms has three maxima: for aromatic hydrocarbons containing 7, 10, and 15 carbon atoms (Fig.5).

The dehydrodimerisation of propene and butadiene over the MoO_3–SiO_2 and WO_3–SiO_2 catalysts has been described[29]. These catalysts exhibited a comparatively high activity in the aromatisation of propene. Thus the selectivity in relation to C_6–C_8 aromatic hydrocarbons reached 33% on the MoO_3–SiO_2 catalyst (treated with HCl) for a propene conversion of 71.4%.

The recently published studies[30,31] whose authors investigated the mechanism of dehydrocyclodimerisation and certain other reactions of piperylene in the presence of modified alumina are of undoubted interest. It was shown that piperylene is converted into n-pentenes as well as alkenylcyclohexenes, C_6–C_9 aromatic hydrocarbons and alkenyl and alkyl derivatives of aromatic C_{10} hydrocarbons on $Al_2O_3.K_2O$ at 500 °C:



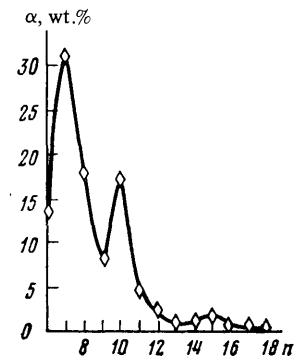


Figure 5. The proportions of aromatic hydrocarbons with different numbers of carbon atoms obtained in the dehydrocyclodimerisation of n-pentane on Pt/Al_2O_3 at 560 °C and for a space velocity of 1.1 h^{-1} (Csicsery[7]); a = overall degree of aromatisation; n = number of carbon atoms in aromatic hydrocarbons.

The activities and selectivities of various oxide catalysts in the dehydrocyclodimerisation of isobutene to *p*-xylene in the non-oxidative version of the reaction have been studied in greatest detail by Japanese workers. Thus the influence of the carrier on the kinetics and mechanism of the vapour-phase dehydrocyclodimerisation of isobutene to xylene over vanadium pentoxide has been studied[32]:

$$2CH_2{=}C\begin{matrix}CH_3\\CH_3\end{matrix} \rightarrow CH_3{-}C_6H_4{-}CH_3 + 3H_2 .$$

In the range 600–800 K at atmospheric pressure the equilibrium constant of this reaction is 4.0–5.4, which corresponds to the equilibrium isobutene conversion in the range 97–100%, i.e. as stated above, the reaction is not limited by the thermodynamic equilibrium.

Together with V_2O_5, the following metal oxides have been used as the active phase: Cr_2O_3, MoO_3, Fe_2O_3, WO_3, and Nb_2O_5 deposited on Al_2O_3 in the atomic proportions M : Al ≅

1 : 19, where M is the metal. Apart from Al_2O_3, the carriers used consisted of SiO_2, Ti_2O_3, MgO, and activated carbon. Data concerning the influence of the nature of the carrier on the catalytic properties of various vanadium oxide catalysts in the dehydrocyclodimerisation of isobutene are presented in Table 1. The V_2O_5/Al_2O_3 catalyst showed the greatest activity under these conditions (at 550 °C the yield of xylene was 27.4% for a selectivity of 54.5%).

Table 1. The influence of the nature of the carrier on the activity and selectivity of vanadium oxide catalysts[32].

Carrier	Conversion, %	Selectivity, %			Yield, %	
		toluene	*p*-xylene	*m*-xylene	iso-octane	n-butane
Al_2O_3 *	49.4	3.2	22.7	31.8	12.0	4.8
SiO_2	25.1	4.0	53.4	5.2	6.5	3.5
MgO	10.8	—	73.2	—	3.0	0.8
Carbon	44.7	2.9	36.9	traces	18.8	—
TiO_2	—	—	—	—	—	—

*Selectivity with respect to benzene 0.6%; yield of *o*-xylene—traces.

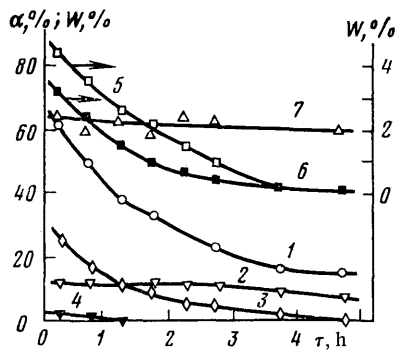


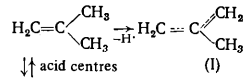
Figure 6. Variation of the degree of conversion α of isobutene (curve *1*) and the yields *W* of *p*-xylene (curve *2*), *m*-xylene (curve *3*), o-xylene (curve *4*), but-2-ene (curve *5*), and but-1-ene (curve *6*) as well as the selectivity in the formation of xylenes (curve *7*) in the presence of the V_2O_5/Al_2O_3 catalyst at 550 °C as a function of the duration of the experiment[32].

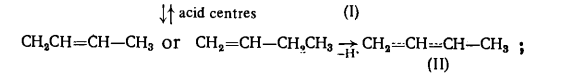
It was established that the catalytic properties of the V_2O_5/Al_2O_3 catalyst change rapidly with time (Fig.6). Thus the *m*- and *o*-xylenes formed in the first hours of the test subsequently disappear and *p*-xylene remains the dominant isomer. The yield of n-butene, formed as a result of the isomerisation of isobutene, also decreases similarly with time, the selectivity of the aromatisation remaining at the same level. Completely different results were obtained in a test of the V_2O_5/MgO catalyst: during the first two hours, the selectivity of the formation of xylene increases from 40 to 75% and remains subsequently at a constant level, the degree of conversion varying only slightly with time and remaining at the level of 10–15%. Skeletal isomerisation does not occur over the catalyst and the only reaction product is *p*-xylene.

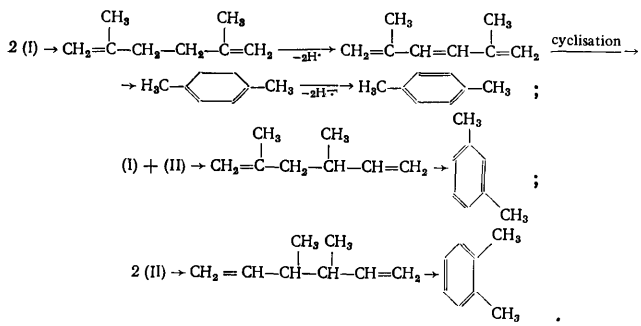
The study of the above oxide carriers for V_2O_5 made it possible to divide them into three groups: (a) aluminium and silicon oxides on which all the xylenes as well as small amounts of benzene and toluene are formed; (b) magnesium oxide and activated charcoal on which only *p*-xylene is formed; (c) titanium dioxide on which an inactive catalyst is obtained.

The virtual absence of the isomerisation of xylenes on the V_2O_5/Al_2O_3 specimens shows that *m*- and *o*-xylenes are not formed as a result of the reactions of *p*-xylene but apparently arise from a parallel reaction involving the isomerisation of isobutene to n-butene and the subsequent dehydrocyclodimerisation of the latter.

A mechanism of the dehydrocyclodimerisation of isobutene has been proposed[32], according to which *p*-xylene is formed via 2,5-dimethylhexa-1,5-diene on V^{3+} centres without the involvement of acid centres; at the same time *m*- and *o*-xylenes are formed on acid centres via 2,4- and 3,4-dimethylhexa-1,5-dienes:







The formation of 2,5-dimethylhexa-1,5-diene and *p*-xylene has been established experimentally. It has been suggested that the intermediates in the formation of *m*- and *o*-xylenes are 2-methylhepta-1,5-diene and octa-2,6-diene. It has been found that in the presence of V_2O_5/MgO the kinetic order of the reaction involving the formation of *p*-xylene is 1.1 with respect to the initial isobutene; the activation energy is 31.4 kJ mol^{-1}. It has been suggested that the rate-limiting stage in the formation of *p*-xylene is apparently the interaction of two adsorbed isobutyl radicals (I).

III. DEHYDROCYCLOTRIMERISATION OF ETHYLENE AND ETHANE TO BENZENE AND OTHER AROMATIC HYDROCARBONS

Together with the dehydrocyclodimerisation of C_3–C_5 olefins and alkanes, the catalytic dehydrocyclotrimerisation of ethylene and ethane with formation of benzene and other aromatic hydrocarbons[11–15,33–35], which has been described comparatively recently, is of undoubted interest. It was shown initially[11,12] that the cyclotrimerisation of ethylene takes place successfully in the presence of Pt/Al_2O_3 in the range 500–670 °C. Subsequently, in the study of catalysts containing other Group VIII metals it was observed that rhodium, ruthenium, iridium, and palladium deposited on alumina (0.5–0.6% of the metal) also catalyse this reaction successfully. In contrast to Pt/Al_2O_3, the cyclotrimerisation of ethylene on these catalysts proceeds at lower temperatures

with appearance of benzene in the reaction products in the presence of the Ru–Ir catalysts already at 450 °C and at 350 °C in the presence of the Rh catalyst.

Thermodynamic calculation showed that the cyclo-oligomerisation of lower olefins, including ethylene, can occur over a fairly wide temperature range[12]. Indeed the equilibrium in the ethylene–benzene system in the range from room temperature to 700 °C and above is almost entirely displaced towards the formation of benzene. Here one should note that the content of benzene in the equilibrium mixture decreases somewhat with increase of temperature. The dehydrocyclo-oligomerisation of other lower hydrocarbons is also thermodynamically feasible over a wide temperature range. Indeed the thermodynamic equilibrium in propene–benzene mixtures at 150–700 °C and in propane–benzene mixtures at 450–700 °C is appreciably displaced towards the formation of benzene. Thus, in the above temperature ranges, the cyclotrimerisation of ethylene as well as the cyclodimerisation of propene and propane are thermodynamically favourable. As regards ethane, its actual aromatisation requires a temperature of ~500 °C. The possibility of the aromatisation of ethane in the presence of platinum and palladium catalysts was demonstrated experimentally by the present author[35].

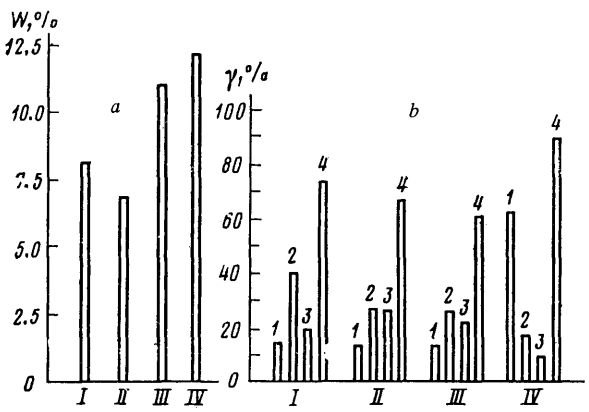


Figure 7. Comparison of the yields (*a*) and selectivities (*b*) in the formation of aromatic hydrocarbons in the presence of a series of catalysts [I) Al_2O_3.F; II) Ru/Al_2O_3.F; III) Pt/Al_2O_3 (AP-56); IV) Rh/Al_2D_3.F] in the cyclotrimerisation of ethylene: 1) benzene; 2) toluene; 3) xylenes; 4) the sum of aromatic C_6–C_8 hydrocarbons; W = overall yield of catalytic reaction products relative to C_2H_4 passed through the system; γ = fraction of aromatic hydrocarbons in the catalytic reaction mixture.

In the course of the study of the cyclotrimerisation of ethylene by a pulsed microcatalytic method platinum/alumina catalysts modified in different ways have been studied in greatest detail[12]. The specimen treated with nitric acid in the course of its preparation proved to be a relatively more active and "low-temperature" catalyst. The yield of aromatic hydrocarbons in its presence reached 9–11% relative to the ethylene passed through the system and 10–14% relative to the ethylene which has reacted. As mentioned above, other Group VIII metals deposited on alumina also exhibited a catalytic activity in the above reaction. The results obtained in the presence of rhodium, ruthenium, and iridium catalysts have been published by Bragin et al.[33] In the course of the application of the first three–four ethylene pulses an increase of the activity of the catalyst was observed; after a definite initiation period the catalytic activity remained close to the maximum in the course of several pulses and then gradually fell.

It has been shown[33,35] that in the presence of M/Al_2O_3 (M = Pt, Ru, Pd, or Ir) catalysts not only ethylene but also ethane undergoes dehydrocyclotrimerisation in the range 550–650 °C with formation of benzene and its homologues. However, the reaction proceeds with somewhat lower degrees of conversion than for ethylene.

The above data refer to the study of the cyclotrimerisation of ethylene under pulsed conditions. Catalysts exhibiting a comparatively high activity and selectivity have also been studied under the conditions of a flow system. Fig.7 presents data[14] referring to the most interesting metal/alumina catalysts. In terms of activity and selectivity, the rhodium- and platinum-containing catalysts proved to be the most effective. The yield of aromatic hydrocarbons in the flow system relative to reacted ethylene reached 18–22%. The presence of C_3–C_6 olefins in the catalytic reaction mixture is striking. It is noteworthy that, in the presence of the rhodium catalyst, cyclotrimerisation takes place at a temperature lower by 80–100 K than on other catalysts; the Rh/Al_2O_3 catalyst has yet another important quality—it exhibits the highest selectivity with respect to the formation of benzene.

It follows from the results of Bragin et al.[14] that in the presence of the 0.6% Rh/Al_2O_3 catalyst the benzene content in the catalytic reaction mixture was 63% and the sum of C_6–C_8 aromatic hydrocarbons was 91%. Specimens with another rhodium content are somewhat less active and are less selective by a factor of 1.5 with respect to the formation of benzene. Nevertheless they are 3–8 times more selective than other metal/alumina systems and Al_2O_3 itself. The distinctive properties of rhodium catalysts discussed above are apparently primarily related to the catalytic properties of rhodium itself, because it is well known that rhodium-containing catalysts are widely used for the demethylation of alkylbenzenes to benzene.

A rhodium/alumina catalyst with a relatively high catalytic activity has been studied by X-ray photoelectron spectroscopy[13]. The state of the metal in the Rh/Al_2O_3 specimen containing 3.5 wt.% of rhodium was investigated as a function of the conditions of the preliminary treatment and the catalytic reaction. It was established that the spectroscopic characteristics of rhodium in the initial non-reduced specimens and in catalysts after oxidative regeneration correspond to the Rh^{3+} state. In the latter case line broadening was observed, which apparently indicates a stronger interaction of rhodium with the carrier.

When the catalyst is treated with hydrogen and also in a hydrocarbon medium, Rh^{3+} is almost completely reduced to zerovalent rhodium. This transition is accompanied by a shift of the spectrum towards lower energies by 3 eV. It has also been noted that the spectrum of reduced rhodium is somewhat broadened compared with that of metallic foil. An important factor is the positive charge observed in the Rh–Al_2O_3 system, appearing when the catalyst interacts with ethylene and its reaction products. It was noted that, under the influence of the reaction medium, the rhodium catalyst is activated in the dehydrocyclotrimerisation of ethylene and that the electronic state of rhodium is then altered. In the course of the activation of the catalyst a positive charge arises on the Rh clusters (formally rhodium passes to the +1 oxidation state); the subsequent decrease of the catalytic activity is accompanied by the return of rhodium to a nearly zerovalent state.

Comparison of the results presented above with the literature data suggested that under certain conditions ethylene can be converted into aromatic hydrocarbons not only in the presence of metal/alumina catalysts but also on alumina itself. Indeed experimental data[33] confirmed this hypothesis. Experiments performed on different γ-Al_2O_3 specimens with different specific activities and also on specimens with and without halogen showed that the cyclotrimerisation of ethylene takes place successfully in the range 500–650 °C. The yield of aromatic hydrocarbons on catalysts with a high acidity is then appreciably higher, which is consistent with the results of a study[23] devoted to the aromatisation of propene in the presence of alumina. Apart from aromatic hydrocarbons, considerable amounts (>25%) of unsaturated aliphatic C_3–C_6 hydrocarbons were detected in the ethylene catalytic reaction mixture. This finding is important for the understanding of the mechanism of the cyclo-oligomerisation of ethylene in the presence of alumina and the above metal oxide catalysts. Studies performed with different alumina specimens free from metal showed that, under the conditions of a flow system, the best results are obtained at 550 °C in the presence of the γ-Al_2O_3 specimen containing 3.4% of fluorine and having a specific surface of 180 $m^2\ g^{-1}$.[33]

The problems of the stability and regeneration of catalysts of the cyclotrimerisation of ethylene merit special attention. An attempt has been made[14] to obtain certain data on the stability of catalysts in a flow system and to determine the conditions for their regeneration. It has been observed that treatment of the catalyst with air for 2 h at 400–450 °C restores its initial activity and selectivity. The catalyst treated periodically in this way after being used for 4–5 h retains its initial activity in the course of 20–30 h. However, it was noted that not all the catalysts investigated are sufficiently stable. Thus the Rh/Al_2O_3 and Pt/Al_2O_3 catalysts are the most stable, while Al_2O_3 itself and Ru/Al_2O_3 are much less stable and somewhat less active after regeneration. The mechanism of the regeneration of catalysts of the cyclotrimerisation of ethylene is so far obscure, but, in conformity with the literature[14,36], one can assume that the regeneration of the metal/alumina catalysts with air consists in burning off and removing from their active surfaces carbon deposits formed on the catalyst in contact with ethylene at 450–550 °C. However, one cannot rule out the possibility that the regeneration of the metal oxide catalyst with air is also associated with a change in the valence state of the active metallic phase.

The mechanism of the formation of aromatic hydrocarbons from ethylene is apparently fairly complex. One of the possible variants is a two-dimensional termolecular reaction on the surface of the catalyst in which a single benzene molecule is formed from three ethylene molecules. An alternative pathway is one in which the formation of aromatic hydrocarbons is preceded by a series of preliminary stages and the cyclotrimerisation reaction is a complex consecutive process. The final answer to these questions is as yet impossible, although the results obtained already constitute definite evidence in support of the second pathway.

The first indication of the course of the reaction is provided by the set of products, indicated above, formed as a result of the cyclotrimerisation of ethylene. Virtually all the catalytic reaction mixtures contain propene and C_4–C_6 aliphatic hydrocarbons; the amount of the latter increases with temperature and with increase of contact time, which is particularly notable on passing from a pulsed to a flow system. Special series of experiments with the initial propene showed that propene is one of the possible intermediates in the aromatisation of ethylene. The yield of aromatic hydrocarbons increased by a factor of ~1.5 when ethylene was replaced by propene[12]. A still more distinctive picture was obtained in a study of the cyclo-oligomerisation of ethylene–butene mixtures (Fig.8) containing 0, 12.5, 25, 50, and 100% of butene in the presence of platinum on fluorinated alumina as the catalyst.

Fig.8 shows that initially the yield of aromatic hydrocarbons, in the first place benzene and toluene, increases appreciable when ethylene is partly replaced by butene, which shows that the formation of butene is apparently an intermediate stage in the cyclotrimerisation of ethylene. The extremum in the dependence of the yields of benzene and toluene on the composition of the reacting gas is consistent with this hypothesis. Presumably, when butene greatly predominates in the initial gaseous mixture, it is converted mainly into xylenes and hydrocarbons with higher molecular weights.

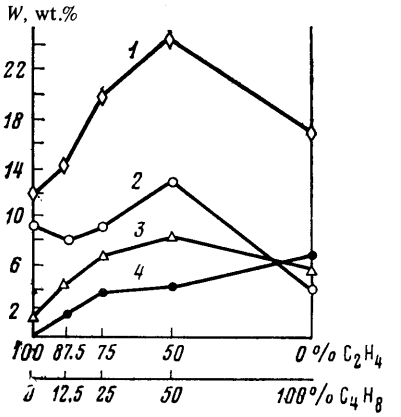


Figure 8. The results of the dehydrocyclo-oligomerisation of ethylene, butene, and their mixtures in the presence of 0.6% Pt/Al_2O_3.F at 559 °C: 1) the overall yield W of aromatic C_6–C_8 hydrocarbons; 2) benzene; 3) toluene; 4) xylenes.

Thus the results support the hypothesis of the preliminary linear oligomerisation of ethylene with formation of C_6 and higher fragments, which is followed by their cyclisation and aromatisation. The proposed mechanism of the cyclotrimerisation of ethylene is also supported by the results obtained independently in a study of the interaction of hydrocarbons with different structures on the surface of fluorinated Al_2O_3 with the aid of diffuse reflectance spectra[37]. Al_2O_3.F, which the present author used previously both as an independent catalyst and as a carrier for various metal/alumina catalysts (M = Pt, Rh, and others) in the cyclotrimerisation of ethylene, was applied. The nature of the spectra and particularly the appearance of a band in the region of 354 nm lead to the hypothesis that surface compounds with conjugated double bonds are formed on alumina. This hypothesis is consistent with the dimerisation of lower olefins on the Al_2O_3 surface with simultaneous evolution of hydrogen known from the literature[38]. These data can be accounted for by the formation of a linear dienyl carbonium ion on the surface; for example, in the case of propene we have

$$H_2C=CH-CH_3+CH_3-CH=CH_2 \rightarrow H_2C=CH-\overset{+}{C}H-CH_2-CH= \\ =CH_2+\bar{H}+H_2\ .$$

The above results permit the conclusion that linear and cyclic oligomerisation of lower olefins, preceding their aromatisation, take place on the surface of Al_2O_3 and even

more so on metal/alumina catalysts. According to this concept, one can assume that the cyclotrimerisation of ethylene consists of a series of consecutive reactions; one of these is the formation of butene and also propene, which undergo oligomerisation, codimerisation, C_5- and C_6-cyclisation, cracking, disproportionation, etc. At the same time one must emphasise that all the above evidence in support of the consecutive ethylene cyclotrimerisation mechanism does not rule out other reaction pathways which apparently make a smaller contribution to the overall ethylene aromatisation process under the conditions which we investigated. The C_6-dehydrocyclisation of long-chain ethylene oligomers formed in the course of the reaction as well as the termolecular catalytic formation of benzene from ethylene, already mentioned above, may be indicated as possible parallel pathways.

Depending on the experimental conditions (and in the first place on the catalyst used), the benzene and its homologues formed in the cyclotrimerisation of ethylene can undergo further reactions For example, a proportion of the toluene and xylenes detected in the catalytic reaction mixture are obtained by the methylation of benzene. The latter can be obtained in its turn by the catalytic demethylation of toluene and xylenes. This possibility has been tested[13] in relation to the platinum and rhodium catalysts as well as Al_2O_3.F and has been confirmed experimentally.

At the same time one can put forward certain considerations also concerning cyclotrimerisation catalysts. As shown above, metal/alumina catalysts, and in the first place those containing platinum and rhodium, proved to be the most effective. The results obtained, and particularly the occurrence of cyclotrimerisation on the surface of alumina itself, indicate a significant influence of the carrier on specific stages of the reaction. Indeed, on the basis of studies of both catalytic and spectroscopic properties of Al_2O_3, one can postulate that the dimerisation and oligomerisation of lower olefins proceed mainly on the acid centres of alumina. These centres are apparently responsible for isomerisation, polymerisation, and also may be partially responsible for coke formation.

Table 2. The results of the conversion of propene on various metal phosphate catalysts.[41]

Catalyst	Conversion of propene (%) with formation of different products		
	CO_2	C_3H_4O	C_6H_6
$Ca_3(PO_4)_2$	17.1	0	0
$CrPO_4$	5.2	0	0
$FePO_4$	31.9	8.5	0
$Co_3(PO_4)_2$	4.8	0	0
$Ni_3(PO_4)_2$	1.7	0.2	0
$Cu_3(PO_4)_2$	39.6	5.1	0
$Zn_3(PO_4)_2$	4.6	0.2	0
$CePO_4$	2.5	0.4	0
$BiPO_4$*	51.0	5.7	23.1
$BiPO_4$**	19.3	19.2	4.5
$2Bi_2O_3 \cdot P_2O_5$	45.0	0	35.4

*Obtained at a high temperature.
**A type of monazite.

It is known that, when fluorine is introduced into Al_2O_3, the catalytic activity of the latter increases in a whole series of reactions, which is as a rule attributed to the appearance of strong protic centres on the Al_2O_3 surface[39]. It is also known that Al_2O_3 (particularly "acid" alumina) exhibits an appreciable catalytic activity in the cyclisation of olefins and dienes with formation of the corresponding cyclanes and cyclenes. Furthermore, Al_2O_3 is also a dehydrogenating agent albeit a relatively weak one. The dehydrogenation reaction on Al_2O_3 is apparently associated with its aprotic centres, capable of abstracting H atoms from the hydrocarbon molecule. The trienes formed as a result of the consecutive dehydrogenation can then undergo further thermal cyclisation.

At the same time the main dehydrogenating component in the metal/alumina catalysts used is undoubtedly the metal and in the first place platinum. Evidently vigorous dehydrogenation of olefins to dienes and of cyclenes to aromatic hydrocarbons respectively takes place on metallic centres. Furthermore, the metallic centres of the catalyst promote a more far-reaching and more selective dehydrocyclisation. The introduction of a metal (platinum and particularly rhodium) into the catalyst increases the hydrocracking properties of the latter. This is apparently the reason (the formation of smaller "fragments" from aliphatic compounds and dealkylation of alkyl- and polyalkyl-benzenes among aromatic hydrocarbons) why the selectivity of the reaction with respect to the formation of benzene and toluene increases appreciably.

IV. OXIDATIVE DEHYDROCYCLODIMERISATION OF LOWER OLEFINS AND ALKANES

This section deals with the second type of dehydroaromatisation of lower olefins and alkanes—the oxidative version with participation of atmospheric oxygen or oxygen forming part of the catalyst. Various compounds, particularly bismuth phosphate, arsenate, and antimonate, as well as the binary mixture of the oxides Bi_2O_3 and SnO_2 are used as catalysts of the oxidative dehydroaromatisation of olefins in the presence of oxygen[40-42]. Instead of the last oxide, one can also use magnesium, titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, zirconium, niobium, silver, silicon, or lead oxides[41,43]. Alkali metal compounds in the form of oxides, hydroxides, or weak acid salts are used as promoting agents. The above oxides can also be employed as deposited catalysts on alumina, carborundum, silica, pumice, graphite, etc. as carriers.

Oxygen-containing and aromatic compounds are formed in the oxidative catalytic dehydroaromatisation of olefins with participation of oxygen in the range 300–600 °C. Propene is then converted into acrolein and benzene; this is accompanied by the formation of CO_2 as well as small amounts of CO, acetaldehyde, and hexa-1,5-diene. Butene gives rise to 2,5-dimethylhexa-1,5-diene, CO, and CO_2; isobutene and butadiene are converted mainly into *p*-xylene.

The oxidative dehydrodimerisation and aromatisation reactions have been used successfully not only in reactions involving olefins but also in those with their functional derivatives, particularly halogenoalkanes, unsaturated amines, cyanides, and alcohols[44]. The reactions can occur in both oxidising and reducing media. The process is usually carried out in a reducing medium when the required products are olefin dimers. We may note that, with increase of the partial pressure of oxygen in the mixture of reacting compounds, the selectivity in the formation of linear and cyclic olefin dimers is appreciably reduced.

The dehydroaromatisation of propene has been studied[41] in the presence of various metal phosphates. Table 2 presents the results of these experiments carried out at 500 °C with a mixture of 9% of propene 18% of oxygen. It is seen from the data in Table 2 that the activities of various phosphates differ markedly. The highest degrees of conversion of propene were achieved in the presence of Bi^{3+} ions. The maximum

yield of aromatic hydrocarbons was reached for the Bi:P = 2:1 ratio; at 500 °C and for the oxygen:propene ≅ 2:1 ratio, ~36% of propene is converted into benzene.

Different temperatures and catalysts apparently have different effects on the selectivity of the reaction. Thus at 300–450 °C in the presence of bismuth arsenate and basic bismuth sulphate, propene gives rise mainly to acrolein while in the range 400–550 °C benzene predominates. Bismuth phosphate, arsenate, and antimonate as well as bismuth titanate and sulphate exhibit a relatively high selectivity with respect to the formation of benzene, while bismuth molybdate is more selective in the reaction involving the conversion of propene into acrolein.

The influence of basic promoting agents on the catalytic properties of tin oxide is significant in the oxidative dehydroaromatisation of propene. Thus oxides with basic properties increase the yield of benzene, while modification of the catalysts by acid oxides favours the formation of acrolein with a simultaneous decrease of the overall activity. The influence of various oxide additives on the catalytic activity of tin oxide in the oxidative dehydroaromatisation of propene at 550 °C has been studied[41].

The study of binary oxide systems such as $Bi_2O_3 + P_2O_5$, $Bi_2O_3 + As_2O_5$, and $Bi_2O_3 + TiO_2$ showed[41] that weakly acid catalysts promote the formation of benzene, while strongly acid catalysts promote the formation of acrolein. The latter include, for example, bismuth molybdate. The following mechanism of the aromatisation of propene has been proposed for the bismuth phosphate catalytic system[40]:

$$2CH_3{=}CH{-}CH_3 \xrightarrow[-2H]{} \underset{(A)}{2CH_2{=}CH{-}CH_2} \xrightarrow[-4H]{} C_6H_6 ,$$

where (A) is an intermediate π-allyl complex. This mechanism is consistent with data[45–47] according to which acrolein and hexa-1,5-diene are also formed (from propene on the acid Bi–P catalyst, Cu_2O, and Ag) via an intermediate π-allyl complex adsorbed on the surfaces of the above catalyst.

The oxidative dehydroaromatisation and dimerisation of propene have also been investigated in other studies[48,49]. The conditions for the dimerisation and aromatisation of propene and isobutene in the presence of the In_2O_3/pumice catalyst in the range 440–550 °C have been described[48] and it has been shown[49] that the dehydrodimerisation of propene to diallyl on lead oxides depends on the composition of the reaction mixture and takes place in a reducing medium. In a reducing medium lead oxides are unstable and they are reduced during the period of the experiment. The reduction of the oxide has a positive effect on the process selectivity. The highest selectivity is shown by the catalyst consisting of PbO and metallic lead in the stationary state.

The metal oxides investigated in the oxidation reactions of lower olefins have been divided[43,50] into four conventional groups. They are represented below by series with decreasing activities:

(1) oxides favouring the formation of acrolein:

$$MoO_3 > Sb_2O_3 > V_2O_5 > TiO_2 = Fe_2O_3 > SiO_2 > WO_3, Al_2O_3;$$

(2) oxides favouring the formation of benzene or hexa-1,5-diene:

$$ZnO > Bi_2O_3 > In_2O_3 > SnO_2 > CdO;$$

(3) oxides favouring the formation of CO_2:

$$CuO = Co_3O_4 > NiO > Cr_2O_3 > MnO_2 = GeO_2;$$

(4) oxides weakly favouring the formation of CO_2:

$$CaO, MgO\ GeO_2, PbO_4, Te_2O_3.$$

Within the framework of this classification, it was noted that the majority of the oxides of the first and second groups are *n*-type semiconductors, while those in the third group are *p*-type semiconductors.

The $Bi_2O_3–Al_2O_3$ catalyst mainly promotes the linear dimerisation of propene and isobutene at 540 °C; the addition of $Cr_2O_3–Al_2O_3$ to the above catalyst promotes the dehydrocyclisation of the dimers formed initially, giving rise to aromatic hydrocarbons. The oxidative dehydrocyclodimerisation of propene to benzene on the following catalysts has also been described: $Bi_2O_3–ZnO$, $Bi_2O_3–WO_3$, and $Bi(SnO_3)_3$. It was assumed[43] that hexa-1,5-diene and cyclohexa-1,3-diene are intermediates in the reaction.

Trimm and coworkers[51–53] described the reactions of propene and isobutene in the presence of indium and thallium oxides. In the presence of the above catalysts, propene is converted into acrolein, hexa-1,5-diene, benzene, and carbon dioxide, while methacroleine, 2,5-dimethylhexa-1,5-diene, *p*-xylene, benzene, toluene, traces of *o*- and *m*-xylenes, and carbon dioxide are formed from isobutene. According to the authors[51–53], benzene and toluene are secondary xylene conversion products. The selectivity in the formation of aromatic hydrocarbons hardly changed with increase of temperature from 480° to 530 °C; at the same time the selectivity in the formation of 2,5-dimethylhexa-1,5-diene increased appreciably under these conditions. The yield of aromatic hydrocarbons can be increased by modifying the catalysts with indium and thallium oxides (already mentioned) or by cyclising the diene formed initially in an additional reactor in the presence of a dehydrocyclising catalyst, for example, chromium oxide.

The study of the reactions of propene and isobutene in the presence of indium oxide in the range 420–500 °C for different ratios of the initial olefin and oxygen showed[52,53] that the proportions of the reaction products depend significantly on the ratio of the hydrocarbon and oxygen. The maximum yield of benzene and hexadiene from propene is attained for the molar ratio $O_2 : C_3H_6 \cong 0.2–0.3$. It has been suggested that hexa-1,5-diene can be formed both on the catalyst surface and in the gas phase at a higher temperature. It has been shown that acrolein and hexadiene inhibit the dehydrocyclodimerisation reaction, while benzene does not have an appreciable influence on the reactions of propene. These findings support the view that the adsorption of propene, acrolein, and hexadiene apparently takes place on centres of the same type, while the dehydrocyclisation of hexadiene to benzene occurs on centres of another type[54]. It has been shown[52,53] that the toluene and benzene formed in the reaction of isobutene are the products of the subsequent transformations of dimethylhexadiene and *p*-xylene. The kinetics of the formation of diene and *p*-xylene in the range 460° to 495 °C have been investigated and virtually identical activation energies, amounting to 126–130 kJ mol^{-1}, have been obtained.

It has been established experimentally[52] that hexadiene and acrolein are the primary reaction products in the formation of benzene and carbon dioxide respectively from propene. According to the authors[52], the above reactions can be described overall by the following stoichiometric equations:

$$2CH_3{-}CH{=}CH_2 + 1/2O_2 \rightarrow CH_2{=}CHCH_2CH_2CH{=}CH_2 + H_2O,$$
$$CH_2{=}CHCH_2CH_2CH{=}CH_2 + O_2 \rightarrow C_6H_6 + 2H_2O,$$
$$CH_3CH{=}CH_2 + O_2 \rightarrow CH_2{=}CH{-}CHO + H_2O.$$

The oxidative dehydrodimerisation of isobutene in the presence of indium oxide proceeds, according to Parera and Trimm[53], with formation of an intermediate π-allyl complex, which dimerises to a diolefin with subsequent cyclisation and aromatisation.

The oxidative dimerisation of propene in the presence of bismuth oxide without the supply of oxygen to the reaction mixture has been studied[55]. The starting materials was a mixture of propene and nitrogen in molar proportions of 2 : 1 at an experimental temperature of 475–560 °C. An increase of temperature entails a decrease of selectivity with respect to hexa-1,5-diene and an increase of selectivity with respect to benzene and CO_2. The hypothetical pathways leading to the formation of hexa-1,5-diene and acrolein from propene have been studied using bismuth oxide and molybdate as oxidants[56]. The authors concluded that bismuth oxide forms surface complexes with propene, which then decompose to hexa-1,5-diene and bismuth compounds.

It has been suggested[55] that propene interacts directly with the oxygen of the crystal lattice of the oxide with formation of water and the reduction of the oxide to the metal. The overall equation is as follows:

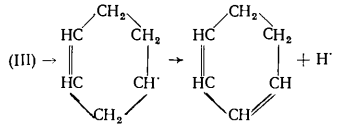
$$2CH_2=CHCH_3+1/2O_2\rightarrow CH_2=CHCH_2CH_2CH=CH_2+H_2O$$

or

$$6C_3H_5\,(g)+Bi_2O_3\rightarrow 3C_6H_{10}\,(g)+2Bi\,(s)+3H_2O\,(g)\,.$$

According to the authors[55], the first stage consists in the formation of a C_3 allyl radical, which then interacts with the oxygen of the lattice after being adsorbed; the subsequent stage involving the dehydrocyclisation of hexa-1,5-diene to cyclodiene takes place with formation of C_6 radicals, which exists in forms (III) and (IV):

$$\underset{\text{(III)}}{CH_2=CH-CH_2-\dot{C}H-CH=CH_2} \rightleftarrows \underset{\text{(IV)}}{\dot{C}H_2-CH=CHCH_2CH=CH_2}\ ;$$



An alternative pathway leading to the formation of hexa-1,5-diene was studied at the same time, taking into account the possibility of the formation of allyl radicals in the pyrolysis of propene. Here two variants are possible (a) the interaction of two allyl radicals on the surface or in the gas phase with formation of hexa-1,5-diene ($2CH_2=CH-\dot{C}H_2 \rightarrow CH_2=CH-CH_2CH_2CH=CH_2$) and (b) the interaction of the allyl radical with propene involving the loss of hydrogen and formation of n-hexenyl or isohexenyl radicals, which then cyclise to methylcyclopentene:

$$CH_2=CH-\dot{C}H_2+CH_2=CH-CH_3\rightarrow\begin{cases}\rightarrow CH_2=CH-CH_2-CH_2-\dot{C}H-CH_3\\ \rightarrow CH_2=CH-CH_2-\underset{CH_3}{CH}-\dot{C}H_2\end{cases}.$$

Analysis of the reaction products enabled the authors[55] to exclude the latter variant of the formation of hexa-1,5-diene, where the allyl radicals adds directly to the propene.

The catalysts of the oxidative dehydroaromatisation of lower olefins (bismuth phosphates) have been studied by X-ray diffraction after their reduction by propene.[57] The main propene reaction products on these catalysts are the same as for the reaction of propene in the presence of oxygen; benzene was obtained in a yield of ~20%. The study of the catalysts showed that after reduction the specimens consist of a mixture of metallic bismuth and bismuth phosphate ($BiPO_4$).

The oxidative dehydrodimerisation and aromatisation of propene in the presence of the individual oxides SnO_2 and Bi_2O_3 as well as the binary oxide system SnO_2–Bi_2O_3 have been recently described[58,59]. The experiments were performed in the absence of oxygen from the gas phase and the oxidative reactions of the hydrocarbons occured with participation of the oxygen in the oxide. It was established that Bi_2O_3 promotes the oxidative dimerisation of propene to hexadiene with a low conversion but with a fairly high selectivity. At the same time SnO_2 exhibits an appreciable catalytic activity in the oxidative dimerisation of propene to hexadiene and the subsequent dehydrocyclisation of hexadiene to benzene in the initial stage of the reduction of the surface of the oxide. The addition of small amounts of one oxide to another increases the oxidising capacity of the catalyst.

The mixed oxide with the ratio Bi : Sn ≈ 1 : 1 exhibits the most effective oxidising properties in the propene dehydrodimerisation and aromatisation reactions. Trimm and Doerr[52] discussed a similar mechanism of the oxidative dimerisation of propene on the SnO_2 surface in terms of the mechanism of the dimerisation of propene in the presence of In_2O_3 on the basis of their experimental data.

The results of a study of the oxidative conversion of propene on a series of individual oxides (copper, nickel, vanadium, cobalt, cadmium, zinc, titanium, iron, antimony, tin, indium, and bismuth oxides) and some of their binary mixtures and also on oxide systems promoted by alkali metal compounds and ammonia have been published[20]. All the above oxides with the exception of Sb_2O_3, SnO_2, and Bi_2O_3 exhibit a high selectivity in the extensive oxidation of propene; copper, nickel, vanadium, cobalt, and iron oxides catalyse the above reactions under the conditions investigated with 100% conversion. On cadmium and antimony oxides, the formation of CO and CO_2 was found to be accompanied by the dehydrodimerisation of propene to diallyl, while on indium oxide propene was dehydroaromatised to benzene, as mentioned above. Bi_2O_3 and SnO_2 are active in both reactions.

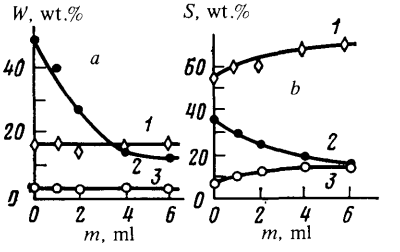


Figure 9. *a*) The influence of the amount of NH_3 (*m*) on the composition of the products (*W*) of the reaction of propene; *b*) the selectivity *S* of the process in the Bi–Ni system at 560 °C; 1) benzene; 2) CO + CO_2; 3) hexa-1,3-diene[20].

In the study of the promoting effect of ammonia and alkali metal compounds on the activity of the bismuth–nickel catalyst it was shown that basic additives appreciably suppress the extensive oxidation reaction and increase the selectivity in the formation of benzene and hexa-1,5-diene. The highest selectivity with respect to benzene is observed when the catalyst is promoted by sodium and rubidium compounds and that with respect to hexa-1,5-diene is attained in the presence of lithium and potassium compounds. Ammonia hardly affects the concentration of benzene and hexa-1,5-diene in the catalytic reaction mixture, but tends to increase appreciably the selectivity in their formation, which rises with increase of the amount of ammonia in the reaction zone with a simultaneous decrease of the amounts of carbon monoxide and dioxide (Fig.9).

Thus it follows from the data presented above that, in the region of the oxidative dimerisation and aromatisation of C_3–C_4 olefins, the reactions of propene and isobutene on indium and bismuth oxides have been studied in greatest detail and most completely and a high activity of the binary oxide catalysts has been discovered. The oxidative conversion of olefins under the conditions of a reducing medium, the influence of promoting additives on the activity of catalysts and the selectivity of their action, and the mechanism of the action of promoting agents have been studied in much less detail.

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During the preparation of the review for the press, a series of studies by foreign[60–65] and Soviet[66–70] workers, devoted to the aromatisation of hydrocarbons (including lower hydrocarbons) in the presence of high-silicon ZSM zeolites, were published. The zeolites, which exhibit a high activity and selectivity in the given process, constitute a new promising generation of zeolite-containing catalysts of the reactions of hydrocarbons and many of their functional derivatives.

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Cytochrome P-450—An Effective Catalyst of the Oxidation of Organic Compounds by Peroxides

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Experimental data on the oxidation of organic compounds by peroxides and other oxidants with participation of cytochrome P-450 from different natural sources are described sytematically and critically. The role of cytochrome P-450 in the oxidative dealkylation of *N*-alkylamines and ethers by hydroperoxides and also its involvement in the peroxide oxidation of aromatic compounds, saturated aliphatic acids, steroids, and other substrates is discussed. Attention is concentrated on the comparison of the mechanism of the oxidation of organic compounds in the complete liver enzyme system, incorporating cytochrome P-450, cytochrome P-450 reductase, and phospholipids as well as NADPH and O_2, and the mechanism of the oxidation of organic compounds by hydroperoxides with participation of cytochrome P-450 alone.
The bibliography includes 147 references.

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I. INTRODUCTION

In 1978, 20 years elapsed since the discovery by Garfinkel[1] and Klingenberg[2] of a unique haemoprotein—cytochrome P-450. This haemoprotein is widely distributed in nature and is a component of enzyme systems belonging to the class of oxidoreductases which have been called mono-oxygenases or mixed-function oxidases. Three years after the discovery of cytochrome P-450 Mason et al.[3] and Hayashi et al.[4] independently discovered a new type of oxidoreductases which obligatorily require the presence of reduced pyridine-nucleotides (NADPH or NADH) and which oxidise various substrates, inserting one oxygen atom in the latter and reducing the other to water:

$$AH + NADPH + H^+ + O_2 \rightarrow AOH + NADP + H_2O ,$$

where AH is the substrate and AOH the substrate oxidation product. In 1964 Omura and Sato[5,6] established that cytochrome P-450 is a *b*-type haemoprotein and is characterised by an atypical absorption band of the carbonyl complex in the reduced state at 450 nm, which gave rise to the name of the protein.

During two decades, considerable advances have been made in the study of mono-oxygenases, their composition, properties, function, and structure. These achievements have been reflected in monographs, collections of papers, reviews, and conference proceedings[7-16]. It is now well known that enzyme systems containing cytochrome P-450 enter into the composition of the microsomal fraction of human and mammalian liver cells and are responsible for the metabolism of steroids, prostaglandins, and an enormous number of xenobiotics—foreign substances entering the organism from the environment, among which there are carcinogens, medicinal drugs, and other substances. A steroid hydroxylating system, similar in properties to the microsomal hydroxylating system of the liver, is localised in the mitochondria of the adrenal cortex and is responsible for key stages in the biosynthesis of steroid hormones in man and mammals. Many strains of bacteria contain hydroxylating enzyme systems with cytochrome P-450 as the terminal oxidase and are capable of oxidising hydrocarbons, heterocycles, and compounds of other classes.

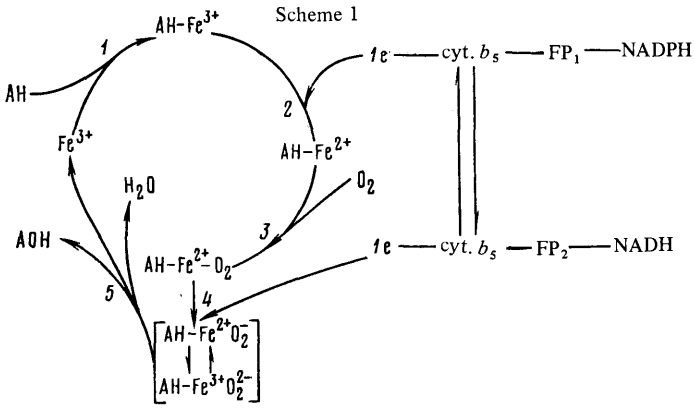
The microsomal hydroxylating system of the liver has particularly attracted the attention of investigators in connection with the significant role of its functions from the point of view of pharmacologists, toxicologists, specialists in chemical carcinogenesis, biochemists, and biophysicists. The microsomal hydroxylating system of the liver consists of three components, each of which has now been isolated and fairly completely characterised[12]: NADPH-cytochrom P-450 reductase (EC 1.6.2.4.), cytochrome P-450 [aryl 4-monoxygenase] (EC 1.14.14.1), and phospholipids. The steroid hydroxylating system from the mitochondria of the adrenal cortex also consists of three main components: adrenodoxin-reductase (EC 1.6.7.1), ferredoxin (adrenodoxin), and cytochrome P-450. The bacterial camphor hydroxylating system also incorporates three enzymes[8]: putidaredoxin reductase, putidaredoxin, and cytochrome P-450_{cam}†.

The mechanism of the action of all three systems is complex and includes many stages. Scheme I presents the sequence of stages in the enzymatic oxidation in the microsomal liver system proposed by Estabrook et al.[17] The majority of these stages have been studied by the methods of stationary and rapid kinetics[18]. The first stage consists in the interaction of the substrate with the oxidised form of cytochrome P-450. The rate constants for this reaction are high and lie in the range 10^2–10^5 litre mol^{-1} s^{-1}.[18] The formation of the enzyme-substrate complex is accompanied by the transition of the

†The following abbreviations have been adopted: cytochrome P-450_{cam} = cytochrome P-450 of camphor hydroxylating bacteria; cytochrome P-450-LM_2 = the form of cytochrome P-450 from the livers of rabbits receiving phenobarbital sodium; PB = phenobarbital sodium; 3-Mech = 3-methylcholanthrene; CHP = cumenyl hydroperoxide; TBHP = t-butyl hydroperoxide; NADPH and NADH can be omitted as they are terms in universal use. AH = substrate in the reduced form.

haem iron from the low-spin to the high-spin state for substrates of type I—hydrocarbons, fully alkylated amines, and unsaturated compounds[19]. The second stage is the reduction of the enzyme–substrate complex by the first electron arriving from the NADPH of the NADPH-specific transport chain via the flavoprotein FP_1 with the possible participation of cytochrome b_5 contained in the membranes of the endoplasmic reticulum of the liver. The second stage consists of two phases: the first phase is characterised by rate constants of 0.2–1 s^{-1} for different substrates and the second (slow) phase is characterised by rate constants in the range 0.09–0.31 s^{-1}.[18]

Scheme 1



The third stage is the formation of the $HA-Fe^{2+}-O_2$ ternary complex. Oxygen adds to the reduced enzyme–substrate complex at high rates of approximately 10^6 mol litre^{-1} s^{-1}.[20] The fourth stage is the reduction of the ternary complex $HA-Fe^{2+}-O_2$ by the second electron, which is believed to be supplied by the NADPH-specific transport chain incorporating the flavoprotein FP_2 and cytochrome b_5. At the present time this reduction stage has not so far been resolved into individual steps for microsomal systems and its rates have not been measured. The fifth stage, which can also be a complex process and can consist of several steps, is characterised by intramolecular reactions of the reduced ternary complex and its decomposition with liberation of a water molecule and a hydroxylated derivative. Cytochrome P-450 is reconverted into the initial form in the fifth stage. Thus the activation of the molecular oxygen in the ternary complex takes place as a result of its reduction by two electrons. The nature of the active form of oxygen responsible for the hydroxylation of chemical compounds of different structure has not so far been established and is controversial.

The mechanism of hydroxylation in the steroid oxidising system and in the camphor hydroxylating bacterial system has, on the one hand, features in common with the oxidation in microsomes and, on the other hand, is characterised by an appreciable difference from the microsomal system[10,11].

The possibility of using organic hydroperoxides for the oxidation of *N*-alkylamines with participation of only cytochrome P-450 in the oxidised form, first discovered by Kadluvar et al.[21], is very important for the study of the mechanism of the activation of molecular oxygen by cytochrome P-450. The use for the hydroxylation of the organic compounds of oxidants containing oxygen already reduced by two electrons (hydroperoxides), $NaIO_4$, $NaClO_2$, and hydrogen peroxide obviates the necessity for the complex electron transport system consisting of macromolecular biocomponents—FP_1, FP_2, and cytochrome b_5.

Thus a possibility arises for simplifying the hydroxylating enzyme system of microsomes by replacing complex components which are difficult to isolate by readily available oxidants. This may be of great importance for the practical application of this unique biocatalyst in the hydroperoxide oxidation of compounds important for pharmacology and medicine. The high capacity of variable-valence metal complexes for the catalytic hydroperoxide oxidation of unsaturated compounds is well known[22,23]: the hydroperoxide oxidation of olefins catalysed by molybdenum complexes constitutes the basis of a familiar method of synthesising epoxypropane developed by the HALCON Company[24].

The aim of the present review is to give a systematic and critical account of reactions involving the oxidation of organic compounds by peroxides with participation of cytochrome P-450 and certain other haemoproteins—haemoglobin, catalase, and cytochrome *c*. We do not consider it necessary to examine here the oxidation of organic compounds by hydrogen peroxide with participation of peroxidases, since peroxide oxidation has been examined in detail in thorough reviews[25,26].

II. OXIDATIVE *N*-DEALKYLATION OF *N*-ALKYLAMINES

The oxidative *N*-dealkylation of alkylamines is one of the commonest reactions catalysed by the microsomal enzyme system. It is believed that this reaction proceeds in two stages, the first of which consists of the insertion of an oxygen atom in a C–H bond of an alkyl substituent with formation of an intermediate hydroxylated compound, which decomposes with liberation of the free amine and formaldehyde:

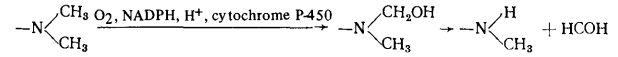


Table 1. The rates of oxidation of amines by pig liver microsomes with participation of cofactors, CHP, and bovine catalase (the rates are given in nanomoles of formaldehyde per minute per miligram of microsomal protein)[21].

Amine	Microsomes, NADPH, O_2	CHP	
		microsomes	catalase
Dimethylaniline	3.4	35.1	451
Aminopyrine	3.5	5.8	312
Benzphetamine	3.3	4.2	10
Propoxyphene	4.7	3.3	0
Ethylmorphine	6.3	2.2	0
Metamphetamine	2.0	0.4	0

The oxidation of aminopyrine, benzphetamine, dimethylaniline, ethylmorphine, and other alkylamines by various peroxides with participation of various animal liver microsomes and highly purified cytochrome P-450 has been investigated[21,27–31]. Table 1 presents data for the oxidation of various amines by cumenyl hydroperoxide (HP) with participation of pig liver microsomes or bovine catalase and compares them with data for the microsomal oxidation of the same substrates in the complete enzyme system containing all the components, NADPH, and O_2.[21] The replacement of the cofactors—NADPH and O_2—by CHP ensures the oxidation of all the amines investigated at rates which in many instances exceed the rate of oxidation in the complete sys-

tem (dimethylaniline and aminopyrine). Catalase is effective only in the oxidation of the first three substrates under the influence of CHP.

The comparison of the efficiencies of various peroxides in the oxidation of the same substrate is of interest (Table 2). The most effective oxidant is CHP. The generation of H_2O_2 in a system containing glucose and glucose oxidase does not ensure high rates of oxidation of aminopyrine. However, comparatively high rates of oxidation of aminopyrine as well as benzphetamine and *p*-nitroanisole by microsomes have been observed in the electrolytic generation of H_2O_2 (or HO_2^-).[28] The participation of cytochrome P-450 in the peroxide oxidation of all amines and many compounds of other classes does not give rise to any doubts. Its involvement has been confirmed by the inhibiting effect of detergents, which convert cytochrome P-450 into the inactive form P-420 (SKF-525A, potassium deoxycholate, etc.)[21] and by the increase of the rate of oxidation of aminopyrine when the microsomes of animals administered phenobarbital are used, since in this case the content of P-450 in the microsomes is significantly increased. The rate of oxidation of aminopyrine by CHP increases in proportion to the cytochrome P-450 concentration. The most convincing demonstration of the direct involvement of cytochrome P-450 in the oxidative dealkylation of amines by peroxides is provided by experiments on the oxidation of benzphetamine involving CHP and highly purified cytochrome P-450 in one of its forms (LM_2) produced in rat liver after induction with phenobarbital[31]. Highly purified cytochrome P-450 is free from reductase, cytochrome b_5, and other components of the microsomal electron transport chains and exhibits a high catalytic activity, which is equal to or exceeds the activity of cytochrome P-450 in microsomes[31].

Table 2. Oxidation of aminopyrine by various peroxides with participation of pig liver microsomes or bovine catalase[21].

Peroxide	Microsomes	Catalase
Cumenyl hydroperoxide	10.8	312
t-Butyl hydroperoxide	3.8	165
Geraniol hydroperoxide	2.0	89
Linoleic acid hydroperoxide	0.7	11
Pregnenolone 17α-hydroperoxide	0.4	8
Di-t-butyl peroxide	0.2	14
H_2O_2-generating system	0.1	0

A detailed kinetic study of the demethylation of many amines by hydroperoxides in the range 20–37 °C has been carried out in our laboratory[27,29,30]. Assuming that the step involving the insertion of activated oxygen in the substrate–cytochrome P-450–ROOH ternary system is rate limiting in the hydroperoxide oxidation of amines and that the subsequent stages involving the liberation of the reaction products are much faster, it is possible to regard the catalytic rate constant as a quantitative characteristic of the decomposition of the ternary complex (Table 3). It follows from Table 3 that the activation energies for the oxidation of amines in hydroperoxide systems (E) are close to the values obtained in the same temperature range and under the same conditions for the complete microsomal system with the cofactors (E^*). The difference between them is within the limits of the error of the determination of the activation energy in a narrow temperature range. The oxidation of amines by hydroperoxides with participation of cytochrome P-450 is characterised by a compensation effect which is described by an equation relating the activation characteristics for the decomposition of the substrate–enzyme–hydroperoxide ternary complex: $\Delta H^*(\text{kcal mol}^{-1}) = 18.7 + 333\Delta S^*$. The compensation effect is characterised by the quantity $\alpha = 333/T_{av} = 1.11$, where T_{av} is the average temperature of the experiments.

Table 3. Parameters of the activation of the enzyme–substrate complexes in the hydroperoxide oxidation of amines with participation of microsomal cytochrome P-450.[29,30]

System	Pre-exponential factor, s^{-1}	E, kcal mol^{-1}	E^*, kcal mol^{-1}	ΔE^a, kcal mol^{-1}
1,2,7-Trimethyldeca-hydro-4-quinolone + CHP	$6.45 \cdot 10^9$	13.7	14.2	+0.5
Dimethylaniline + TBHP	$7.76 \cdot 10^{10}$	15.8	—	—
Aminopyrine + CHP	$1.12 \cdot 10^9$	12.7	13.4	+0.7
Aminopyrine + CHP[b]	$3.30 \cdot 10^8$	12.0	—	—
Monomethylaniline + CHP	$1.95 \cdot 10^{11}$	16.1	16.6	+0.5
Dimethylaniline + CHP	$5.12 \cdot 10^8$	12.2	13.4	+1.2

Note. [a] $\Delta E = E^* - E$; [b] experiments performed with microsomes of rats receiving phenobarbital.

III. THE HYDROPEROXIDE *O*-DEALKYLATION OF ETHERS

The complete microsomal hydroxylating system in the presence of the cofactors NADPH and O_2 catalyses the oxidative *O*-dealkylation of ethers via the mechanism

$$R{-}OCH_3 \xrightarrow{O_2} R{-}OCH_2OH \rightarrow R{-}OH + HCOH \ .$$

In peroxide systems these reactions are carried out by microsomes in the absence of NADPH and O_2.[32–35]

Table 4. Comparison of the rates of the NADPH-dependent and CHP-dependent *O*-dealkylation in catalysis by rabbit PB-microsomes at 22–25 °C (the rates are expressed in nanomoles of aldehydes per minute per milligramme of microsomal protein)[35].

Substrate	With participation of NADPH and O_2	With participation of CHP
7-Ethoxycoumarin	1.5	3.6
p-Nitroanisole	2.3	12.0
Norcodeine	6.2	6.2
Phenacetine	2.3	2.7

Cumenyl hydroperoxide is effective in the *O*-dealkylation of many substrates (Table 4) and in the oxidation of *p*-nitroanisole the rate of reaction exceeds by a factor of 6 the rate of oxidation in the complete system. *O*-Dealkylation is greatly inhibited by sodium dodecyl sulphate and 1-(2-isopropylphenyl)imidazole[32]. Superoxide dismutase hardly affects the rate of *O*-dealkylation, i.e. the reaction does not involve the active radical-anions O_2^-. It is extremely important that haemin, catalase, horseradish peroxidase, and myoglobin are completely inactive in the reactions involving *O*-dealkylation by hydroperoxides[32].

A detailed kinetic study of the *O*-dealkylation of 7-ethoxycoumarin in the range 0–45 °C and of anisole and *p*-chloroanisole in the range 20–37 °C with participation of CHP and microsomes has been carried out[34,35] (Table 5).

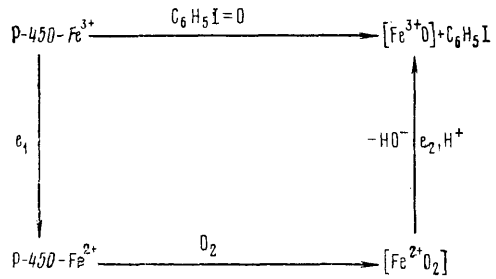
Table 5. Characteristics of the *O*-dealkylation of ethers by cumenyl hydroperoxide[34,35].

Substrate	System	k_0, s^{-1}	E, kcal mol^{-1}	Refs.
Anisole	CHP + intact microsomes	$2.0 \cdot 10^7$	11.4	[34]
p-Chloroanisole	CHP + intact microsomes	$5.5 \cdot 10^7$	11.8	[34]
7-Ethoxycoumarin	CHP + PB-microsomes	—	17.0	[35]

The hydroperoxide oxidation of the same substrate can be achieved via two pathways[34]: TBHP and microsomes demethylate anisole (20%) and at the same time hydroxylate it in the *p*-position (80%) with formation of *p*-methoxyphenol.

For the understanding of the mechanism of oxidation with participation of peroxides and cytochrome P-450, it is of interest that 7-ethoxycoumarin can be *O*-dealkylated by iodosobenzene with participation of microsomes[33], since iodosobenzene contains only one oxygen atom. Presumably the active species attacking the substrates contains only one oxygen atom. Such a species can be the oxenoid complex $[FeO]^{3+}$ (Scheme 2). Scheme 2 illustrates the pathways leading to the formation of the $[FeO]^{3+}$ species by the reaction with iodosobenzene and also in the complete microsomal system.

Scheme 2



IV. HYDROXYLATION OF AROMATIC COMPOUNDS AND EPOXIDATION OF CYCLOHEXENE

A number of studies have been made of the hydroxylation of aromatic compounds by hydroperoxides with participation of liver microsomes and highly purified cytochrome P-450 [36–46] (Table 6).

The hydroxylation of aromatic compounds is accompanied by the decomposition of CHP with formation of cumenyl alcohol. It has been shown[36] that one *p*-aminophenol molecule is formed for each CHP molecule decomposing in the oxidation of aniline. Haemin, catalase, horseradish peroxidase, myoglobin, cytochrome b_5, and cytochrome P-420 are ineffective in the hydroxylation of aniline by cumenyl hydroperoxides[36].

The kinetic characteristics of the hydroxylation of naphthalene by cumenyl hydroperoxide with participation of different enzyme systems have been compared quantitatively[38]. The rate of reaction in the presence of the enzyme system induced by phenobarbital sodium increases in proportion to the increase of the concentration of cytochrome P-450. The catalytic rate constant in induction by 3-methylcholanthrene is reduced by a factor of two compared with the intact systems due to the formation of a new form of haemoprotein (cytochrome P-448) in 3-Mech-induced systems.

Table 6. Comparison of the rates of oxidation of aromatic substrates in the presence of NADPH and O_2 as cofactors and CHP (the rates are expressed in nanomoles of reaction products formed per minute in miligrams of microsomal protein).

System	Substrate	NADPH and O_2 cofactors	CHP
Rat liver microsomes	biphenyl	0.60	1.70
Rat liver microsomes	benzopyrene	0.78	0.89
Rabbit liver PB-microsomes	coumarin	0.062	0.055
Rabbit liver-3- Mech-microsomes	aniline	0.51	50.0

Table 7. The energy characteristics of the oxidation of naphthalene, aniline, and cyclohexene by hydroperoxides.

System	t, °C	E, kcal mol^{-1}	Refs.
Naphthalene			
Male rat PB-microsomes + CHP	5–40	18.8	42
Highly purified rabbit liver cytochrome P-450 (13 nmol/mg of protein) + CHP	5–38	17.2	42
Aniline			
Intact male rate microsomes + CHP	10–40	18.1	42
Male rat PB-microsomes + CHP	5–36	21.3	42
Intact female rat microsomes + CHP	15–37	15.3	40, 41
Intact female rat microsomes + TBHP	15–37	14.5	40, 41
Rat liver cytochrome P-450 (4.4 nmol/mg of protein) + CHP	14–37	15.8	39
Cyclohexane			
Intact male rat liver microsomes + TBHP	20–37	8.15	29

The kinetics of the hydroxylation of naphthalene and aniline by hydroperoxides over a wide temperature range and of the epoxidation of cyclohexene by cumenyl hydroperoxide have been studied in detail[29,37–46]. All the experiments were performed under the conditions involving saturation with respect to the hydroperoxide. The temperature variation of the maximum rates of oxidation of aniline, naphthalene, and cyclohexene obeys the Arrhenius equation, from which the process activation energies were calculated (Table 7). The activation energies for the oxidation of naphthalene by microsomes and highly purified cytochrome in the reaction with the same hydroperoxide are similar. The activation energies for the oxidation of aniline to *p*-aminophenol catalysed by male rat microsomes and purified cytochrome P-450 also differ a little—15.3 and 15.8 kcal mol^{-1}.[39,40,41] Induction by phenobarbital hardly affects the energy characteristics of the oxidation of naphthalene and aniline by cumenyl hydroperoxide[42].

Thus cytochrome P-450 in microsomes and highly purified cytochrome P-450 in solution do not exhibit energy differences in reactions involving the oxidation of the same substrate (naphthalane or aniline) by hydroperoxides. It is therefore of interest to investigate the influence of individual phospholipids on the reactivity of highly purified cytochrome P-450 in the hydroperoxide oxidation of aromatic compounds[43-46], since phospholipids are components of microsomal membranes and are necessary for the reconstruction of the microsomal system for the restoration of its full activity.

The hydroxylation of naphthalene and aniline by cumenyl hydroperoxide with participation of the highly purified LM_2 form of cytochrome P-450 from rabbit liver PB-microsomes (16.8 nmol/mg of protein) has been studied in the presence and absence of various phospholipids[44-46] and it has been shown that the total microsomal phospholipids (TPL), phosphatidylinositol (PI), and lysophosphatidylcholine (LPC) increase the rate of oxidation of naphthalene in the reaction with CHP by a factor of 3–4 when the molar ratio lipids : cytochrome P-450 is 30 and more. Phosphatidylcholine (PC) and sphingomyelin (SM) hardly affect the oxidation of naphthalene up to lipid : cytochrome P-450 ratios of 200–300. The addition of aliphatic acids to the incubation mixture retards the oxidation of naphthalene by cumenyl hydroperoxide.

The addition of TPL, PI, PC, and LPC increases also the rate of oxidation of aniline in the reaction with CHP by a factor of two, PC and SM do not influence the oxidation of aniline, while aliphatic acids retard this process. Thus acid phospholipids (PC, PI, and TPL), containing acid lipid components, activate cytochrome P-450 in the hydroperoxide oxidation of naphthalene and aniline, while lipids existing in the zwitterionic form do not affect the rate of oxidation of a type I substrate (naphthalene) and a type II substrate (aniline)[44-46]. Thus the interaction of cytochrome P-450 with acid lipids affects the rates of hydroperoxide oxidation of aniline. Phosphatidylcholine—the principal component of the microsomal membrane—hardly affects this process. It may be that this factor actually explains the absence of a difference between the activation energies for the hydroperoxide oxidation of naphthalene and aniline with participation of highly purified cytochrome P-450 and membrane-bound cytochrome P-450.[39-42]

The activation of cytochrome P-450 by acid phospholipids in the hydroperoxide oxidation reaction can be accounted for by the stabilisation of the active conformation of the haemoprotein in solution when the lipid molecules are immobilised on the surface of the protein. Coon et al.[47] showed that the interaction of the LM_2 form of cytochrome P-450 with phospholipids is accompanied by an increase of the α-helix content. The spectroscopic changes recorded by differential spectrophotometry in the interaction of LM_2 cytochrome P-450 with phospholipids at different temperatures permit the conclusion that phospholipids can influence the equilibrium involving the spin forms of cytochrome P-450 differing in their ability to interact with substrates of this enzyme[48]. The general considerations concerning the stabilisation of the cytochrome P-450 conformation on interaction with phospholipids can be made specific: cytochrome P-450 assumes the α-helix conformation and can undergo a change in the spin state as a result of conformational rearrangements.

V. OXIDATION OF SATURATED COMPOUNDS AND STEROIDS

Microsomal hydroxylating systems of the liver and kidney, incorporating cytochrome P-450, are known to catalyse the ω-oxidation of aliphatic acids[49,50], the oxidation products being ω1- and ω2-hydroxy acids[50,51]. It has been suggested that liver microsomes contain a highly specific cytochrome P-450 responsible solely for the oxidation to ω1-hydroxy-derivatives, as well as another non-specific cytochrome P-450 which catalyses the ω2-oxidation of aliphatic acids and the hydroxylation of many medicinal drugs and other xenobiotics[51-54]. Kidney microsomes probably contain only one form of cytochrome P-450, which is responsible for both ω1- and ω2-oxidation of aliphatic acids[55,56]. The ratio of the ω1- and ω2-oxidation products is determined by the length of the alkyl substituent in aliphatic acids.

Table 8. Hydroxylation of steroids with participation of rat liver microsomes and different oxidants[60].

Main reaction products	Reaction rates*		
	NADPH, and O_2	$NaIO_4$	CHP
Androstenedione			
6α-OH	0.58	3.97	0.85
7α-OH	0.13	7.13	0.65
15-OH	0.13	0.90	0.12
16α-OH	0.27	0.58	0.43
17β-hydroxy-4-androstene-3,16-dione	0.12	0.70	0.10
Total	1.23	13.28	2.15
Testosterone			
6β-OH	0.74	2.20	1.22
7α-OH	0.34	3.98	0.25
16α-OH	0.16	0.71	0.17
Total	1.24	6.99	1.64
Progesterone			
2α-OH	0.23	0.62	0.12
6β-OH	0.47	1.20	0.48
7α-OH	0	0.44	0
15α-OH	0	0.22	0
15β-OH	0	0.26	0.14
16α-OH	0.41	0.44	0.26
Total	1.11	3.18	1.00
17β-Oestradiol			
Total**	0.38	4.77	1.02

*The rates are given in nanomoles of product formed per minute per miligram of protein.
**The overall data for 6α-OH, 6β-OH, and 16α-OH are indicated.

Cumenyl hydroperoxide and liver microsomes ensure the oxidation of lauric acid to an ω2-hydroxyacid, the ω1-hydroxy-derivative not being formed in detectable amounts[57], while in the complete system containing the cofactors NADPH and O_2 the formation of ω1- and ω2-hydroxy-derivatives in proportions of 1 : 5 is observed. Kidney microsomes and CHP ensure the ω2-oxidation of lauric acid at low rates, but ω1-hydroxy-lauric acid was not detected in this instance[57]. Thus oxidation of lauric acid by CHP with participation of liver and kidney microsomes can yield the same product in both instances—ω2-hydroxylauric acid. This fact confirms the existence in the liver microsomal fraction of two or more forms of cytochrome P-450 responsible for the ω-oxidation of aliphatic acids. Presumably cytochrome P-450 responsible for the ω2-oxidation of aliphatic acids by cumenyl hydroperoxide is identical in liver and kidney microsomes[57].

Rat liver microsomes catalyse the oxidation of aliphatic acids by oxidants such as sodium chlorite, sodium periodate, iodosobenzene, and iodosobenzene diacetate[58]. The oxidants employed hydroxylate aliphatic acids only in the ω2-position

and are much more effective than NADPH and O_2 in the complete microsomal system; iodosobenzene diacetate is the most effective substance. The ω2-oxidation of laurate with participation of liver microsomes is inhibited by a substrate of the microsomal system (aniline), which fully arrests the process[58].

A number of studies have been made on the peroxide oxidation of steroids with participation of cytochrome P-450-containing systems[59-65]. The peroxide oxidation of steroids can be catalysed by liver microsomes[60], cytochrome P-450 from adrenal cortex mitochondria[62], and cytochrome P-450 from liver microsomes[59,63]. Table 8 presents data on the oxidation of steroids in the full microsomal system and also in the presence of $NaIO_3$ and CHP.[60] Evidently the use of $NaIO_3$ and CHP in combination with liver microsomes does not ensure the selective oxidation of steroids, which can be attributed to the presence of many forms of cytochrome P-450 in liver microsomes or to the possible role of radicals in the oxidation, which frequently leads to the absence of selectivity. $NaIO_3$ is the most effective oxidant for steroids[60]; $NaClO_2$, CHP, pregnenolone 17 α-hydroperoxide, t-butyl hydroperoxide, and linoleic acid hydroperoxide give rise to lower rates of oxidation than in the complete system with participation of NADPH and O_2. Oxidants such as H_2O_2, $K_2Cr_2O_7$, CrO_3, $KClO_4$, $KBrO_3$, K_2IrCl_6, and $NaIO_3$ exhibit no activity in the oxidation of steroids with participation of liver microsomes[60].

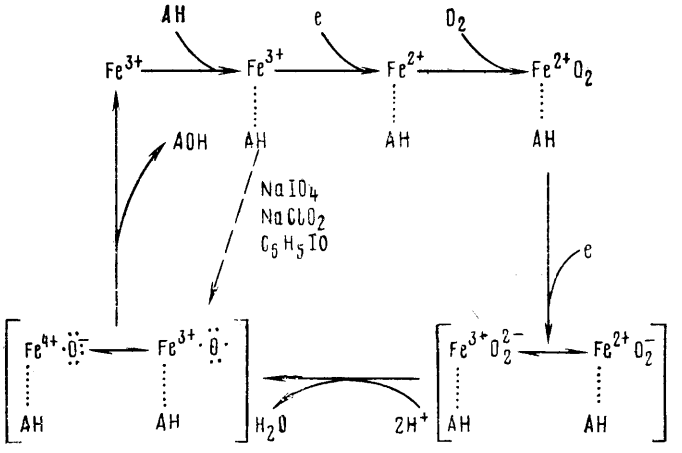
The partly purified cytochrome P-450 from rat liver microsomes oxidises androstenedione when $NaIO_4$, $NaClO_2$, H_2O_2, and organic hydroperoxides are used[59]. Sodium periodate is the most effective oxidant. It is noteworthy that horseradish peroxidase, catalase, and metmyoglobin do not exhibit catalytic properties in the oxidation of steroids by various peroxides[59].

The study of the oxidation of androstenedione by various iodobenzene derivatives with participation of cytochrome P-450 from liver microsomes showed[64] that the effectiveness of the oxidant diminishes in the sequence 2-nitroiodosobenzene diacetate > 2-chloroiodosobenzene diacetate > 2-methoxyiodosobenzene diacetate 4-methyliodosobenzene > iodosobenzene. The effectiveness of the oxidant is determined by several factors: the tendency towards its oligomerisation, which diminishes when the oxidant is coordinated to haem iron, the presence of substituents in the 2-position, and the electron-donating capacity of the substituents. The rates of 7α-, 6β-, and 16α-hydroxylation of androstenedione by 2-nitroiodosobenzene diacetate are higher by factors of 108, 130, and 167 than the corresponding values for the oxidation of this substrate in the same positions in the complete microsomal system. The authors[64] believe that this finding supports the view that there are different rate-limiting stages in the oxidation of androstenedione in the complete microsomal system and in the reaction involving peroxides.

The majority of oxygen donors used in the oxidation of steroids do not ensure process selectivity, in contrast to the observations made in the ω-hydroxylation of saturated aliphatic acids[57,58]. However, in the oxidation of cholesterol by $NaIO_4$ and CHP in the presence of liver microsomes, exceptional selectivity is observed: both oxidants ensure the exclusive 25-hydroxylation of cholesterol[65]. It is of interest to note that, in the oxidation of cholesterol in the complete microsomal system with participation of NADPH and O_2, hydroxylation takes place in the 6β-, 7α-, 12α-, 25-, and 26-positions[65]. In this case the transition to peroxide oxidation is characterised by a greater reaction selectivity. This finding is difficult to account for unambiguously, although one can postulate that competition between the oxidants and cholesterol for binding to cytochrome P-450 renders all the substrate positions except the 25-position inaccessible to attack by the hydroxylating agent. The effectiveness of highly purified cytochrome P-450 in the oxidation of androstenedione by sodium periodate increases following the addition of phosphatidylcholine: the rate of 6β-hydroxylation of this substrate increases by a factor of 2.5 for a cytochrome P-450 : lipid ratio of approximately 10.[63] Detergents such as Triton X-100 also exert an activating effect on cytochrome P-450 in the oxidation of androstenedione by sodium periodate[63].

Hrycay and coworkers[59-62] believe that the active oxidant in the hydroxylation of steroids by various peroxides is the same species, namely the ferryl ion $[Fe^{4+}O^-]$, which is formed when oxygen donors (ROOH, $NaIO_4$, $NaClO_2$, etc.) interact with oxidised cytochrome P-450 (Scheme 3). The postulated species is analogous to the well known complex I (see Scheme 3) formed in the interaction of hydrogen peroxide with peroxidases or catalases[25,26].

Scheme 3



One of the alicyclic compounds oxidised by hydroperoxides with participation of microsomes or purified cytochrome P-450 is cyclohexane[66,31]. In this case the hydroperoxide system (TBHP) is less effective than the complete microsomal system. The affinity of cyclohexane for cytochrome P-450 in the presence of TBHP decreases by a factor greater than 2 and the rate of oxidation falls by a factor of approximately 10.[66]

In conclusion of this section of the review, one should note that both liver microsomes and pure cytochrome P-450 are effective catalysts of the oxidation of saturated compounds such as aliphatic acids and cyclohexanes. It is significant that these compounds are not oxidised at appreciable rates at temperatures close to physiological values by oxidants such as hydroperoxides, hydrogen peroxide, and $NaClO_2$. Cytochrome P-450 accelerates the oxidation of saturated compounds by peroxides. This finding is particularly important from the standpoint that the strength of the C–H bonds at which oxidation occurs is high compared with compounds of other classes (90–95 kcal mol^{-1}). Nevertheless the oxidation of saturated compounds by readily available oxidants with participation of cytochrome P-450 at 20–37 °C is strikingly easy.

VI. PEROXIDASE REACTIONS OF CYTOCHROME P-450

Reactions catalysed by peroxidases are characterised by the following stoichiometry:

$$AH_2 + XOOH \rightarrow A + H_2O + XOH ,$$

where AH_2 is the hydrogen donor and XOOH the peroxy-compound. In 1972 Hrycay and O'Brien[67] showed that cytochrome P-450 exhibits the properties of peroxidases and reduces steroid hydroperoxides to the corresponding alcohols in the presence of a hydrogen donor such as *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPPD). The peroxidase activity of rat liver and borine adrenal cortex microsomes in relation to steroid peroxides is analysed in Table 9.[67] In all cases the rat liver microsomes are more active than the bovine adrenal cortex microsomes.

Table 9. The peroxidase activity of microsomes in relation to steroid hydroperoxides*[67].

Hydroperoxide	Rat liver microsomes	Bovine adrenocortical microsomes
Progesterone 17α-hydroperoxide	92	31
Pregnenolone 17α-hydroperoxide	80	30
Allopregnanolone 17α-hydroperoxide	76	27
Linoleic acid hydroperoxide	75	25
Cumenyl hydroperoxide	34	12
Cholesterol 7β-hydroperoxide	30	17
Cholest-4-en-3-one 6β-hydroperoxide	30	10
Cholesterol 7α-hydroperoxide	22	9
Cholesterol 25-hydroperoxide	17	9
Cholesterol 26-hydroperoxide	15	9
Cholesterol 20α-hydroperoxide	12	5

*The peroxidase activity was measured at 23 °C in 3 ml of phosphate buffer (pH 7.5) containing 0.2×10^{-3} M TMPD, 2 mg of microsomal protein, 0.05×10^{-3} M hydroperoxides, and 1.5×10^{-3} M EDTA.

The peroxidase activity is not influenced by CO, nitrogen, EDTA, and 2-phenyl-2-propanol. Sodium azide has a slight inhibiting effect (20%). The peroxidase activity diminishes by 95% when the microsomes are heated to 80 °C. Substrates of the microsomal enzyme system exert an effective inhibiting influence on the peroxidase reactions of liver microsomes[67]: type I substrates—androstenedione, testosterone, 17β-oestradiol, aminopyrine, hexabarbital, and linoleic acid—inhibit the peroxidase reactions by 65–34%, while type II substrates—aniline, imidazole, pyridine, cyanide, corticosterone, and n-octylamine—inhibit the peroxidase activity by 83–50%. This confirms that cytochrome P-450 is involved in the peroxidase reactions in the oxidised form. The peroxidase activity of cytochrome P-450 from adrenal cortex microsomes is also largely inhibited by substrates of microsomal systems of both types[67].

In the peroxidase reactions of cytochrome P-450, NADH and NADPH can function as hydrogen donors[68]. The combined experimental data[67,68] show that the peroxidase activity is characteristic of the oxidised form of P-450: CO does not inhibit the peroxidase reactions of cytochromes P-450, because it forms a complex solely with the reduced form of this haemoprotein. It has been suggested that, when cytochrome P-450 reacts with hydroperoxides, a complex is formed[25,26] in which the haem iron can exist in a high oxidation state:

$$\text{P-450—Fe}^{3+} + \text{ROOH} \rightarrow \text{P-450—Fe}^{5+} + \text{ROH} .$$

It is known that primary aliphatic alcohols are not substrates of peroxidases[69]. However, rate liver microsomes and highly purified cytochrome P-450 catalyse the oxidation of primary aliphatic alcohols to aldehydes[70]. The susceptibility of alcohols to oxidation by cumenyl hydroperoxide with participation of cytochrome or catalase diminishes with increase of the size of the aliphatic group[70].

Cytochrome P-450 is the most effective catalyst of the oxidation of ethanol by cumenyl hydroperoxide, while cytochrome *c*, haemoglobin, and peroxidase hardly catalyse the oxidation of alcohol. The induction of microsomes by phenolbarbital sodium increases by a factor of almost 5 their catalytic activity in the oxidation of ethanol by CHP.[70] The mechanism of the oxidation of aliphatic alcohols with participation of cytochrome P-450 and hydroperoxides is controversial: alcohols can behave as hydrogen donors and can be oxidised via the peroxidase mechanism, which has already been discussed in this section; the second possibility in the oxidation of alcohols is associated with the monooxygenase activity of cytochrome P-450—the insertion of an activated oxygen atom from the P-450–ROOH complex in an alcohol molecule with subsequent decomposition of the unstable intermediate to acetaldehyde and water:

$$CH_3CH_2OH \xrightarrow{\text{cytochrome P-450-ROOH}} \rightarrow \left[CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—OH \right] + \text{P-450} + \text{ROH}$$
$$\downarrow$$
$$CH_3CHO + H_2O .$$

The mechanism of the oxidation of alcohols by hydroperoxides with participation of cytochrome P-450 has never been studied. The reduction of steroid hydroperoxides by cytochrome P-450 is of great interest for the elucidation of the mechanism of the oxidation of steroids by liver microsomes and in their biosynthesis with participation of mitochondrial cytochrome P-450 from adrenal cortex, since steroid hydroperoxides can behave as intermediates which are then converted into hydroxy-derivatives with participation of cytochrome P-450.

An undesirable side process accompanying the hydroperoxide oxidation of the majority of substrates is the degradation of cytochrome P-450 by hydroperoxides[43–45,71,72]. It has been shown[72] that CHP and TBHP decompose not only cytochrome P-450 but also cytochrome b_5, which plays an important role in electron transport in microsomal chains. The hydroperoxide of linoleic acid decomposes cytochrome P-450 in the microsomal form when this haemoprotein has not been induced, or has been induced by phenobarbital or 3-methylcholanthrene[71]. According to Jeffery et al.[71], two phases—rapid and slow—can be observed in the degradation of microsomal cytochrome P-450. A detailed kinetic study of the degradation of cytochrome P-450 by cumenyl hydroperoxide in microsomes and after purification to different extents in solution has shown that this process is complex and consists of three stages[43–45]. Under the conditions of an excess of CHP, the degradation of cytochrome P-450 can be characterised in terms of bimolecular rate constants for each degradation stage. The extent of the first stage in the degradation of cytochrome P-450 depends on the initial concentration of the hydroperoxide and on the duration of the degradation process regardless of the degree of integration of the cytochrome (microsomes or solubilised cytochrome P-450).[43–45]

Table 10 presents the kinetic parameters characterising the degradation of cytochrome P-450 and its reaction with CHP at different stages of this process. The rate constant k_0 (s^{-1}) characterises the degradation of cytochrome P-450 in the absence of hydroperoxide. This reaction is observed at 25 °C in only one case—for cytochrome P-450 in the LM_2

form when its specific content is 12.0 nmol/mg of protein. The substrates of the microsomal system (aniline and others) greatly inhibit the degradation of cytochrome P-450 by hydroperoxides. The introduction of a radical process inhibitor (1-naphthol) into the incubation mixture entails its consumption and marked inhibition of the degradation process. The inhibiting effect of this antioxidant confirms the radical mechanism of the degradation of cytochrome P-450. The complex of the hydroperoxide and cytochrome P-450, whose structure will be discussed in the next section of the review, decomposes with formation of active radicals:

$$[P-450-Fe^{3+}\ldots OOR] \rightarrow [P-450-Fe^{2+}] + \dot{O}OR + H^+ ;$$
$$[P-450-Fe^{2+}] + ROOH \rightarrow [P-450-Fe^{3+}] + HO^- + RO^\cdot .$$

Table 10. Kinetic parameters of the three stages of the degradation of cytochrome P-450 in the reaction with cumenyl hydroperoxide at 25 °C.[43-45]

System	Specific content of cytochrome P-450, nmol g^{-1}	k_0, s^{-1}	K_I	K_{II}, litre mol^{-1} s^{-1}	K_{III}
Intact rat microsomes	0.61	0	18.50	1.80	0.23
Rat PB-microsomes	1.70	0	41.00	1.24	0.22
Rabbit PB-microsomes	2.10	0	8.77	0.47	—
Rat 20-Mech-microsomes	1.00	0	12.67	1.53	0.33
Cytochrome P-450-LM_2**	12.00	$3.0 \cdot 10^{-4}$	0.78	0.43	0.15
" "	13.00	0	0.60—0.97*	0.12—0.39*	0.07
" "	16.84	0	0.69	0.10—0.59*	0.16
Cytochrome P-450-LM_4**	9.40	$0.17 \cdot 10^{-4}$	0.18—0.42*	0.10—0.22*	0.11

*Rate constants for hydroperoxide concentrations in excess of 3.0×10^{-4} M.
**From rabbit PB microsomes.

The radical species RO· and RO_2^- formed attack the porphyrin ring of the cytochrome P-450 haem and the apoenzyme, decomposing the latter.

VII. CATALYSIS OF THE PEROXIDE OXIDATION BY OTHER HAEMOPROTEINS (HAEMOGLOBIN, CATALASE, AND CYTOCHROME *c*)

The elucidation of the catalytic activities of other haemoproteins in the peroxide oxidation is of great interest. Cytochrome P-450 cannot be replaced in all cases by other more readily available haemoproteins: the oxidative dealkylation of *N*-alkylamines is catalysed by horseradish peroxidase in combination with H_2O_2,[73] and by haemoglobin and catalase in combination with CHP or H_2O_2;[74] the oxidation of aniline by cumenyl hydroperoxide is catalysed by haemoglobin[75] and cytochrome *c*;[76] haemoglobin exhibits a peroxidase activity in the presence of H_2O_2 in relation to phenylhydrazine[77].

Data on the catalytic activity of haemoproteins in various reactions are summarised in Table 11. Only cytochrome P-450 is catalytically active in all the reactions, while other haemoproteins can catalyse only one or several peroxide oxidation reactions. None of the haemoproteins, except cytochrome P-450, is capable of catalysing the peroxide *O*-dealkylation of ethers[32] and the oxidation of steroids[59]. Catalase participates in the oxidation of alcohols[70] and in the *N*-dealkylation of amines[21]. Cytochrome P-420 does not exhibit an activity in any of the reactions[32]. It is important to note that the mechanisms of reactions with participation of cytochrome P-450 and other haemoproteins are as a rule different. Hitherto radicals have not been detected directly in any of the peroxide oxidation reactions involving cytochrome P-450. On the other hand, the reactions involving the oxidative *N*-dealkylation of amines in the H_2O_2–peroxidase[73], CHP–catalase, and CHP–haemoglobin[74] systems are accompanied by the formation of radicals. Radical process inhibitors (1-naphthol and others) retard the oxidation of aniline in the haemoglobin–CHP and cytochrome *c*–CHP systems[75,76], which indicates the presence of radical stages in these instances.

Table 11. Catalytic properties of haemoproteins in the oxidation of the organic compounds by peroxides and certain other non-peroxide oxidants.

Reaction	Haemoproteins with catalytic activity*	Refs.	Haemoproteins without catalytic properties	Refs.
N-Dealkylation of amines	cytochrome P-450 (ROOH, H_2O_2)	21, 27-31	cytochrome P-420	21
	catalase (ROOH, H_2O_2)	21		
	peroxidase (H_2O_2)	73		
	haemoglobin (CHP, H_2O_2)	74		
O-Dealkylation of ethers	cytochrome P-450 (CHP, TBHP, C_6H_5IO)	32-35	haemin, catalase, peroxidase, myoglobin, cytochrome P-420	32
Hydroxylation of aromatic compounds	cytochrome P-450 (ROOH, H_2O_2)	28, 36-46	haemin, catalase, peroxidase, myoglobin, cytochrome b_5, cytochrome P-420	36
	haemoglobin (CHP)	75		
	cytochrome *c* (CHP)	76		
Oxidation of steroids	cytochrome P-450 (ROOH, $NaIO_4$, C_6H_5IO, $NaClO_2$)	59-65	peroxidase, catalase metmyoglobin	59
Oxidation of alcohols	cytochrome P-450 (ROOH, H_2O_2)	70	peroxidase, cytochrome *c*, haemoglobin	70
	catalase (ROOH. H_2O_2)			

*The oxidants employed are indicated in brackets.

Table 12. The efficiencies of various systems involving the demethylation of dimethylaniline (0.003 M) at 37 °C in terms of the concentrations of haemoproteins (10^{-6} M).[74]

System	$10^7 w_0^*$, mol litre s^{-1}
Catalase (5.0×10^{-7} M) + CHP (0.001 M)	26.60
Haemoglobin (2.0×10^{-6} M) + CHP (0.003 M)	2.60
Haemoglobin (2.0×10^{-6} M) + H_2O_2 (0.006 M)	4.10
Cytochrome P-450 in microsomes (1.25×10^{-6} M) + CHP (0.001 M)	8.20

*Initial rate of reaction.

In the oxidative dimethylation of aminopyrine in the H_2O_2–peroxidase system radical species have been detected by EPR and are apparently aminopyrine radical-cations[73]. The oxidation of aminopyrine by peroxidase in combination with H_2O_2 is the most effective method for transforming this compound compared with other systems.

The efficiencies of various haemoproteins in the peroxide oxidation of dimethylaniline are compared in Table 12.[74] Catalase is most effective in the peroxide oxidation of dimethylaniline. The inhibiting effect of 1-naphthol has been observed only in reactions involving cytochrome P-450.[74]

At 37 °C in a phosphate buffer (pH 7.4) aniline is hydroxylated to *p*-aminophenol in the haemoglobin–CHP system. Kinetic[75] and spectroscopic[78,79] data show that the hydroxylation of aniline entails the formation of a complex of haemoglobin with aniline and the hydroperoxide: difference spectra of the aniline–haemoglobin system are characterised by an absorption maximum at 425 nm and a minimum at 405 nm.[78] Identical differential spectra have been observed in the interaction of haemoglobin with CHP. The reaction involving the insertion of activated oxygen takes place in the aniline–haemoglobin–CHP ternary complex. A side reaction involving the degradation of haemoglobin by cumenyl hydroperoxide is observed in the course of the process[75].

At 0 °C cytochrome *c* catalyses in combination with CHP the oxidation of aniline to *p*-aminophenol. Aniline forms a complex with cytochrome *c* characterised by an absorption maximum at 420 nm and a minimum at 401 nm at pH 5.8 in a phosphate buffer. Complexes of CHP with cytochrome *c* are formed, which is reflected in the difference absorption spectra, having a maximum at 433 nm and a minimum at 413 nm.[76] 1-Naphthol inhibits the oxidation of aniline by cumenyl hydroperoxide with participation of cytochrome *c*,[76] but does not arrest it completely.

The ability of haemoglobin in combination with H_2O_2 to exhibit a peroxidase activity has been demonstrated[77] in relation to the oxidation of phenylhydrazine in this system. It has been suggested that oxidised haemoglobin (Hb^{3+}) forms a complex with H_2O_2, which decomposes and generates ferrylhaemoglobin, the latter oxidising phenylhydrazine:

$$Hb^{3+} + H_2O_2 \rightarrow [HbO]^{4+} + H^+ + {}^1/_2H_2O_2,$$
$$2[HbO]^{4+} + C_6H_5NH{-}NH_2 \rightarrow 2Hb^{3+} + C_6H_5{-}N{=}NH + H_2O.$$

Table 13. Spectroscopic characteristics of complexes of haemoproteins with hydroperoxides.

System, conditions	λ_{max}, nm	λ_{min}, nm	References
Rabbit PB-microsomes–CHP; pH 7.4	441, 535	422, 579	[81]
Rat liver microsomes–TBHP; pH 7.5; 20°	380–440	418	[82]
Rat liver microsomes–tetralyl hydroperoxide; pH 7.5; 20°	380–440	420	[82]
Cytochrome P-450 from rat liver microsomes–CHP; pH 7.4; 20°	380, 440	418	[39]
Cytochrome P-450–LM_2 from rabbit liver PB-microsomes–CHP	370, 436, 540	421	[83, 84]
Haemoglobin–CHP; pH 8.0; 20°	423	405	*
Cytochrome *c*–CHP; pH 5.8; 20°	433	413	[76]

*Data obtained by E.I.Tishenko in the author's laboratory.

The haemoprotein recently isolated from peas differs from cytochrome P-450 and oxidises a number of substrates via the peroxidase mechanism in the presence of hydroperoxides and H_2O_2: indole is oxidised to indoxyl, phenol is oxidised to hydroquinone, α-naphthol is oxidised to α-naphthohydroquinone, and aniline is oxidised to phenylhydroxylamine[80]. The oxidation of indole in the presence of this haemoprotein is slightly inhibited by KCN and NaN_3, but is very markedly retarded by α,α′-bipyridyl, aniline, and *N*,*N*-dimethyl-*p*-phenyldiamine. The new catalyst, was called the "H_2O_2 reducing haemoprotein[80]. The products formed in the oxidation of the substrates enumerated above with participation of this haemoprotein differ greatly from the products of the microsomal oxidation of the same substrates, which confirms the difference between the new haemoprotein and cytochrome P-450.

In conclusion of this section, it must be emphasised yet again that all the reactions catalysed by cytochrome P-450 are accelerated by other haemoproteins. The most significant difference between the catalytic activities of cytochrome P-450 and other haemoproteins is the absence of radical stages in the case of cytochrome P-450 and their presence in the reactions involving other haemoproteins. Peroxides form complexes not only with cytochrome P-450 but also with other haemoproteins; however, the complexes of cytochrome P-450 and other haemoproteins react via different pathways.

VIII. THE MECHANISM OF THE ACTION OF CYTOCHROME P-450 IN THE PEROXIDE OXIDATION OF ORGANIC COMPOUNDS

Cytochrome P-450, haemoglobin, and cytochrome *c* form complexes on interaction with hydroperoxides[81–84]. The formation of complexes by cytochrome P-450 in a microsomal suspension with cumenyl hydroperoxide was first demonstrated spectrophotometrically[81]. When CHP was mixed with liver microsomes from rabbits receiving phenobarbital, difference absorption spectra were recorded at 5 °C with maxima at 441 and 535 nm and minima at 422 and 579 nm. Analogous spectral changes were observed also in the interaction of microsomes with t-butyl and tetralyl hydroperoxides[82] and also in the interaction of purified cytochrome P-450 with CHP.[39]

The interaction of hydroperoxides and peracids with the highly purified LM_2 form of cytochrome P-450 from rabbit liver microsomes has been studied spectrophotometrically in combination with the stopped flow method[83,84]. Difference absorption spectra were obtained with maxima at 370, 436, and 540 nm and a minimum at 421 nm. The interaction of CHP with P-450-LM_2 is described schematically as follows:

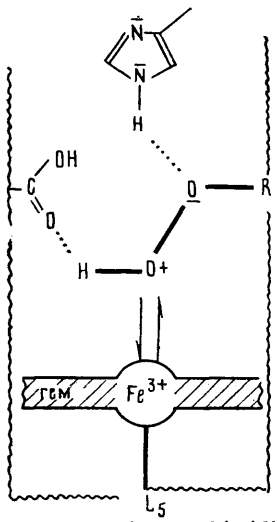
$$P{-}450{-}LM_2 + CHP \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C \underset{k_4}{\overset{k_3}{\rightleftharpoons}} D,$$

where C is the Michaelis complex between CHP and P-450, and D is the spectroscopically detectable species, which can be an oxyferryl derivative of cytochrome P-450. The interaction of CHP and P-450 is very rapid: $k_1 = 5000$ litre $mol^{-1} s^{-1}$. The rate constants for the reverse reaction are $k_2 = 50\ s^{-1}$, $k_3 = 1.3\ s^{-1}$, and $k_4 = 0.009\ s^{-1}$.[83] The kinetic parameters determined for this reaction depend little on the pH and on the addition of phospholipids.

Similar spectra characteristics have been obtained in the study of the products of the reaction of P-450-LM_2 with peracetic, *m*-chloroperbenzoic, and *p*-nitroperbenzoic acids as well as other peroxides. The fact that different peroxycompounds form complexes with P-450 having analogous spectroscopic characteristics suggests that the active species arising on complex formation is similar for different oxidants. The spectroscopic parameters of the complexes of haemoproteins with hydroperoxides are presented in Table 13. According to the author, the formation of complexes by hydroperoxides takes place as shown in Scheme 4. The complex is formed by the undissociated form of the hydroperoxide, one oxygen atom of which (from the HO group) is bound to the haem iron, while the other atom forms a hydrogen bond with histidine; the alkyl residue of the peroxide interacts with the apoenzyme via hydrophobic binding. The distal histidine is probably involved in the stabilisation of the haemoglobin complex. Complexes of haemoglobin with

molecular oxygen are known to be stabilised by the distal histidine[85,86].

Scheme 4



L_5 = cysteinyl or histidinyl.

The spectroscopic characteristics (Table 13) probably refer to the product of the conversion of the complex illustrated in Scheme 4 into the oxyferryl derivative, formed as a result of the dissociation of the –O–O– bond and analogous to complex I, known to occur in the reactions of peroxidases:

$$[Fe^{3+}\cdot\ddot{O}\cdot] \rightleftharpoons [Fe^{4+}\ddot{O}:] \xrightarrow{H^+} Fe^{4+}OH\ .$$

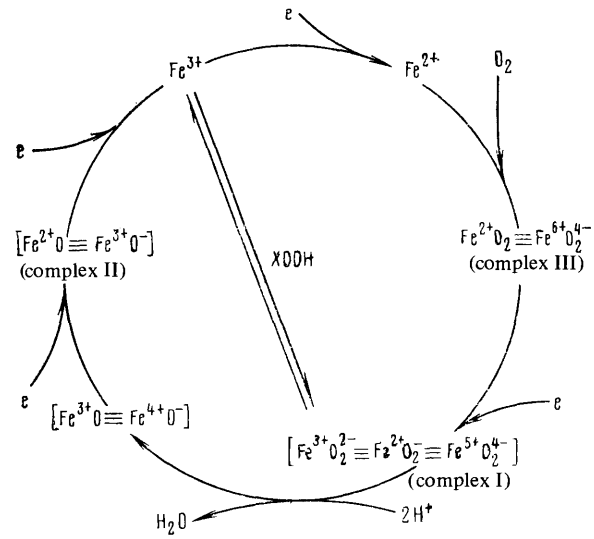
In the interaction of CHP with cytochrome P-450 a signal with a *g*-factor of approximately 2.0, analogous to the EPR signal arising in the interaction of H_2O_2 with metmyoglobin or with cytochrome *c* peroxidase[87,88], was recorded by EPR.[81] It is suggested that this EPR signal is associated with the highest valence states of haem iron, for example, the ferryl 4+ state. When CHP or H_2O_2 is added to metmyoglobin, an EPR spectrum similar to that recorded in the microsomes–CHP system is observed[81]. Yamazaki et al.[89] suggested an overall mechanism which describes the oxidation-reduction reactions of haemoproteins and is distinguished by five valence states of haem iron. This mechanism describes the results obtained in the study of peroxidase and catalase and agrees with the results of the study of the interaction of peroxides with metmyoglobin[90,92].

Scheme 5 illustrates the successive formation of various oxygen-containing species in the functioning of cytochrome P-450 and draws an analogy with the species formed in the functioning of peroxidases. The ternary complex comprising reduced cytochrome P-450, the substrate, and oxygen is equivalent to complex III of peroxidases, as suggested by Ulrich and Staudinger[93]. The valence state of the iron in this complex depends on the distribution of electrons between the oxygen and the iron ion. The one-electron reduction of this complex leads to the formation of complex I or the perferryl ion[89]. The complex I formed can be reduced by a single electron to complex II or simultaneously by two electrons to the initial state (Fe^{3+}–P-450).

Thus the active species formed in the interaction of oxidised cytochrome P-450 with peroxides or in the successive reduction of the substrate–cytochrome P-450–O_2 ternary complex by two electrons can be the same as complex I, which is characterised by a high degree of oxidation of the iron ion.

Complex I can react, receiving in succession one electron from the substrate and being reconverted into the initial form Fe^{3+}–P-450. This peroxidase reaction pathway is characterised by the intermediate formation of complex II. In other cases complex I can obtain immediately two electrons from the substrate and be reconverted into the initial form Fe^{3+}–P-450. This pathway obtains in hydroxylation reactions believed to involve an oxenoid mechanism[93]. The relative contributions of the peroxidase and oxenoid reactions of complex I are determined primarily by the nature of the haemoprotein. In reactions involving hydroperoxides, haemoglobin and cytochrome *c* react via the peroxidase pathway with the intermediate formation of radicals, which has been confirmed by the retarding effect on these reactions by radical process inhibitions. The oxenoid or hydroxylase mechanism is characterised by the absence of radical stages, which is confirmed by the effect of the same inhibitors in hydroxylase reactions[74].

Scheme 5



Complex I, which exists in different forms ($Fe^{2+}O_2^-$, $Fe^{3+}O_2^{2-}$, $Fe^{3+}O$, $Fe^{4+}O^-$) contains oxygen in the triplet or singlet state. The singlet oxenoid inserts an oxygen atom into the substrate via a three-centre synchronous mechanism with formation of a singlet reaction product:

$$\rangle C{-}H + [:\ddot{O}\,Fe^{3+}] \rightarrow \left[\rangle C\overset{OFe^{3+}}{\cdots}H\right] \rightarrow \rangle C{-}OH + Fe^{3+}\ .$$

If the oxenoid is in the triplet state, then the direct insertion of oxygen in the substrate is impossible, because this reaction would be spin-prohibited. In this case oxidation proceeds via the "abstraction of a hydrogen atom–recombination" mechanism or via a latent radical mechanism, which may not be sensitive to the action of radical process inhibitors:

$$\rangle C{-}H + [\cdot\ddot{O}\cdot Fe^{3+}] \rightarrow \rangle C^{\cdot} + [H\ddot{O}\cdot Fe^{3+}] \rightarrow \rangle C{-}OH + Fe^{3+}\ .$$

The different states of the oxygen in complex I can be determined by the nature of the fifth ligand of the haem iron in haemoproteins. The presence of histidine in the fifth position in haemoglobin and cytochrome *c* probably determines significantly the peroxidase reaction pathway with participation of these haemoproteins and hydroperoxides. The cysteinyl group in the fifth position of cytochrome P-450

is responsible for the difference between the spectra of the complexes of this haemoprotein with hydroperoxides and the spectra of the complexes of other haemoproteins (Table 13) and for the hydroxylase reaction pathway.

We shall now consider the possible reaction pathways for the complexes of haemoproteins with hydroperoxides. As a result of the interaction of haemoproteins with hydroperoxides, a Michaelis complex C is formed in which the hydroperoxide is coordinated to the central iron ion via the oxygen atom of the hydroxy-group (see Scheme 4). Evidence for the involvement of the HO groups of cumenyl hydroperoxide in coordination to cobalt and nickel chelates has been obtained by NMR from the chemical shifts of the HO protons in the hydroperoxide[94]. The Michaelis complex C decomposes via reaction (2) with formation of an oxenoid complex or an oxyferryl derivative analogous to complex I. Complex I can react via the hydroxylase mechanism [reaction (3)]. It can receive two electrons in succession from a suitable substrate: the reduction by the first electron leads to the formation of complex II via reaction (4). The Michaelis complex C can decompose in the absence of the substrate with formation of the peroxy-radical $RO_2^{\cdot}$ [reaction (5)]. In this reaction the hydroperoxide behaves as a reductant#:

$$L_5Fe^{3+} + ROOH \rightleftharpoons [L_5Fe^{3+}\ldots \underset{H}{OOR}] \quad (1)$$

(complex C)

$$C \rightarrow [L_5Fe^{3+}O] + ROH \quad (2)$$

(complex I)

$$[L_5Fe^{3+}O] + AH \rightarrow L_5Fe^{3+} + AOH \quad (3)$$

$$[L_5Fe^{3+}O] + AH \rightarrow [L_5Fe^{2+}O] + A^{\cdot} + H^+ \quad (4)$$

(complex II)

$$[L_5Fe^{3+}\ldots \underset{H}{OOR}] \rightarrow L_5Fe^{2+} + H^+ + RO_2^{\cdot} \quad (5)$$

$$L_5Fe^{2+} + ROOH \rightarrow L_5Fe^{3+} + RO^{\cdot} + HO^- , \quad (6)$$

where AH is the substrate and L_5 is the axial ligand in the fifth position.

The reduced form of the haemoprotein is oxidised by another hydroperoxide molecule with formation of the radical $RO^{\cdot}$ [reaction (6)]. Reactions (5) and (6) are well known in the interaction of CHP with metal ions and metal complexes as the Haber–Weiss reactions[95]. The ratios of the rates of reactions (3)–(6) are determined by the nature of the haemoprotein, particularly by the nature of the axial ligand in the fifth position, by the presence or absence of substrates, by the nature of the oxidised substrate, and by other factors. Complex I, formed in the interaction of cytochrome *c* or haemoglobin with cumenyl hydroperoxide, reacts mainly via the peroxidase pathway [reaction (4)], while complex I of cytochrome P-450 reacts mainly via the hydroxylase pathway [reaction (3)]. It is noteworthy that the Michaelis complex C, which is capable of oxidising the substrate in a single stage on interaction with the latter, can serve as the hydroxylating agent. The study of model systems has shown that two hydroxylation mechanisms are possible—consecutive two-state hydroxylation [reactions (2) and (3)] or a single-stage transfer of active oxygen to the substrate[96,97] with the aid of complexes analogous to the Michaelis complex C.

In the presence of substrates or radical process inhibitors, reactions (5) and (6), initiating the degradation of haemoproteins, take place at lower rates. In the absence of substrates or inhibitors, the radicals $RO^{\cdot}$ and $RO_2^{\cdot}$ attack the haem and the apoenzyme and irreversibly decompose them.

The oxygenated form of reduced cytochrome P-450 from liver microsomes was first detected spectrophotometrically by Estabrook et al. in 1971.[17] Gunsalus et al.[98] and Ishimura et al.[99] demonstrated spectroscopically the formation of a complex of molecular oxygen with reduced cytochrome $P\text{-}450_{cam}$, which hydroxylates camphor. The camphor–cytochrome $P\text{-}450_{cam}$–O_2 and reduced cytochrome $P\text{-}450_{cam}$–O_2 complexes have been isolated chromatographically[100,101] below 0 °C in mixed aqueous organic solvents and have been characterised spectroscopically and kinetically. The camphor–cytochrome $P\text{-}450_{cam}$–O_2 ternary complex undergoes autoxidation; the activation energy for this process is 18 kcal mol^{-1} in water and 19 kcal mol^{-1} in an aqueous organic medium[100].

Using the stopped flow method, the formation of a complex of highly purified cytochrome P-450 from liver microsomes with molecular oxygen was investigated spectrophotometrically[102]. In the presence of benzphetamine, this reaction is characterised by two phases: complex A—an oxygenated complex of cytochrome P-450 having maxima at 430 and 450 nm in the difference spectrum—is formed initially. The short-lived complex A is then converted into complex B with a maximum at 440 nm. The formation of complexes of O_2 with reduced cytochrome P-450, can be described schematically as follows:

$$P\text{-}450^{red} + O_2 \overset{k_1}{\rightarrow} \text{complex A} \overset{k_2}{\rightarrow} \text{complex B} \overset{k_3}{\rightarrow} P\text{-}450^{ox}.$$

Complex B has spectroscopic characteristics close to those of complex I and is probably similar to the latter. The reactants are characterised by the following Soret bands: $P\text{-}450^{red}$—424 nm, $P\text{-}450^{ox}$—418 nm, complex A—423 nm, and complex B—421 nm.[102] The rate-limiting stage of the process is the oxidation of cytochrome P-450 in the ternary complex accompanied by the hydroxylation of the substrate. The addition of cytochrome b_5 to the system increases the rate constant k_3, i.e. cytochrome b_5 plays the role of an effector in the reaction.

Thus an oxygenated complex of cytochrome P-450 with properties similar to those of complex I is formed in the complete microsomal system as a result of a series of steps (see Schemes 2, 3, and 5). This complex can transfer an oxygen atom to the substrate with a simultaneous liberation of a water molecule or can initially abstract a water molecule and be converted into the ferryl derivative [$Fe^{3+}O \rightleftharpoons Fe^{4+}O^-$], which transfers an oxygen atom to the substrate.

It is of great interest to elucidate the nature of the rate-limiting stage in the oxidation of substrates in the complete microsomal system. This complex process consists of at least five steps (see Schemes 1 and 5). A kinetic analysis of each of the five steps has been carried out in a review[18], where data obtained in several laboratories were surveyed. Direct measurements of the rate constants for the interaction of substrates with cytochrome P-450, for the reduction of the enzyme–substrate complex by the first electron, and for the formation of the ternary complex comprising reduced cytochrome P-450, the substrate, and oxygen have shown that all three steps are characterised by high rate constants and cannot be rate limiting in the oxidation reaction in the complete system[18].

The rate of this process can be limited either by the reduction of the ternary complex by the second electron or by the step involving the insertion of activated oxygen in the substrate, which is accompanied by the rupture of the attacked bond and subsequent rapid liberation of the reaction product.

#It is noteworthy that the peroxy-radical $RO_2^{\cdot}$ may be bound in a complex, as shown[23] for the decomposition of complexes of hydroperoxides with molybdenum(VI):

$$[Mo^{6+}\ldots \underset{H}{OOR}] \rightarrow [Mo^{5+}\ldots {}^{\cdot}OOR] + H^+ .$$

Hitherto the conversion of the ternary complex, involving its reduction by the second electron and the subsequent decomposition with formation of the reaction product, has not been resolved into individual stages. However, there are experimental facts showing that the rate-limiting stage of the reaction involves the dissociation of the attacked C–H bond in the substrates. The primary isotope effects in the oxidation of substrates in the complete microsomal system have been measured in a number of studies[103–117]; the results are summarised in Table 14. As a rule, high primary isotope effects are observed except for the oxidation of deuterated cyclohexane, for which an isotope effect has not been observed[105]. Studies in which an intramolecular determination has been made of isotope effects involving substrates which are symmetrical and contain simultaneously non-deuterated and deuterated C–H bonds attacked in the oxidation process, such as, for example, 1,3-diphenylpropane-1,1-d_2, are of special interest[114]. In this case the isotope effect is 11. The same value was obtained in the hydroxylation of norbornane in a reconstructed enzyme system of rabbit liver microsomes[117]. The isotope effects obtained leave no doubt that the rate-limiting stage of the oxidation reaction involves the dissociation of the attacked C–H bond, which supports the "abstraction–recombination" mechanism.

Table 14. The primary isotope effects in the microsomal oxidation of various substrates.

Substrate	Isotope effect	References
CD_3-morphine	1.4	103
[α-D_2]Ethylbenzene	1.8	104
[D_{12}]cyclohexane	1.0	105
[11-D_2]Lauric acid	3.0	106
[9-D_2]Caproic acid	3.0	106
Saturated compounds	1.4	107
[16α-D]Pregnenolone	3.0	108
[7α-^{3}H]Taurodeoxycholic acid	3.8	109
[α-D_2]Isopropylamphetamine	1.6	110
CD_3-*o*-nitroanisole	2.0	111
CD_3-methoxyanisole	10.0	112
Aromatic benzene derivatives	1.3–1.75	113
[1,1-D_2]1,3-Diphenylpropane	11.0	114
Biphenyl	1.4	115
N,N'-Dimethylphentermine	1.4	116
Norbornane	11.5	117

Another piece of evidence for the decisive role of the strength of the bond ruptured in the oxidation process is the existence of the so-called uncoupling compounds—fully fluorinated hydrocarbons which interact with cytochrome P-450 but are not oxidised, since the strong C–F bond cannot be ruptured by the oxidising species[118–121].

Comparison of the energy characteristics of the oxidation of the same substrates in the complete microsomal system and in systems containing only cytochrome P-450 and hydroperoxides showed that in both cases the activation energies for the same substrate are similar or identical (see Table 3 and Akhrem and coworkers[29,30]). This comparison, carried out under rigorously identical conditions for both systems (complete and shunted), supports the occurrence of the same rate-limiting stage in the process in both instances. In the hydroperoxide system there is no need for the transfer of the second electron to the enzyme–substrate–hydroperoxide complex, since the oxygen in this complex is already activated by two electrons, i.e. the ternary complex is not reduced in this case and the rate-limiting stage of the reaction can be only the insertion of an oxygen atom with dissociation of the bond in the substrate oxidised. Consequently the same rate-limiting stage of the process can be postulated in the hydroperoxide system and in the complete microsomal system, namely the insertion of active oxygen in the substrate with subsequent rapid decomposition of the complex and liberation of the reaction product.

Data have been obtained[58–62] showing that the use of oxidants ($NaIO_4$, $NaClO_2$, and iodosobenzenes) in combination with cytochrome P-450 makes it possible to increase the rate of transformation of substrates compared with those attained in the complete system. This led the authors to the view that the rate-limiting stages in the two systems are different[58–62]. Here one should note that the difference between the rates of oxidation can be accounted for not by the difference between the rate-limiting stages in the two cases but by different concentrations of the active oxidising species, which is due to the different affinities of molecular oxygen and the oxidants used for cytochrome P-450.

Naturally the most convincing evidence for the nature of the rate-limiting stage in the oxidation process in the complete microsomal system may be provided by the direct measurement of the rates of all the stages of the process by high-speed kinetic methods. Such a study has been performed for the demethylation of benzphetamine in a reconstructed microsomal system[122]. The rate-limiting stage in the oxidation of benzphetamine may be associated with the reduction of the ternary complex by the second electron or with any process involving the transformation of the ternary complex after its reduction, since all the preceding stages are much faster than the accumulation of the reaction products[122,123].

It is noteworthy that under certain conditions in the microsomal membrane the reduction of cytochrome P-450 by the first electron may be the rate-limiting stage of the oxidation reaction. Below 18–20 °C, the interaction of cytochrome P-450 in microsomes with its reductase (flavoprotein I) is hindered due to a change in the phase state of the phospholipids of the microsomal membranes from the liquid crystal state above 18–20 °C to the crystalline state below these temperatures. The phase transition of the membrane phospholipids is reflected in the activation energy for the oxidation of substrates in the complete system: at 18–20 °C a break is observed in the Arrhenius relation for the maximum rates of oxidation or for the catalytic constants[35,42,124]. The activation energy for the oxidation of substrates of the first type above 18–20 °C is 8–12 kcal mol^{-1} and probably refers to the transformation of the ternary complex; the activation energy below 18–20 °C is 18–24 kcal mol^{-1} and refers to another rate-limiting stage, which may be the reduction of cytochrome P-450 by its reductase under the conditions of hindered contact between them. This contact is facilitated when the state of the membrane changes above 18–20 °C as a result of the possibility of the lateral mobility of its components.

IX. PROSPECTS FOR PRACTICAL UTILISATION

In view of the important functions of hydroxylating enzymes it is desirable to search for ways of using them in practice. At the present time only the first attempts have been made at the practical application of monooxygenases containing cytochrome P-450. The region where cytochrome P-450 and its analogues can be used is extremely wide. The enzyme systems of micro-organisms and yeasts containing

cytochrome P-450 can oxidise virtually all hydrocarbons to alcohols: the American firm Mobil Oil took out a patent in 1967 for the oxidation of petroleum hydrocarbons of all classes by monooxygenases present in bacteria of different strains[125].

"Metabolic reactors" for the investigation of the optimisation of medicinal preparations and also for the extracorporeal detoxidation of blood by oxidising the impurities contained in it can be created on the basis of immobilised cytochrome P-450.[126-128] The cytochrome and its analogues in the immobilised state can be used for the selective oxidation of physiologically active compounds, in the first place steroids and certain amines[129]. It is already possible to quote an example of the successful application of monooxygenases in the sphere of traditional applications of the activity of microbial cells—steroid chemistry; thus Mosbach[130,131] converted Reichstein's substance "S" into prednisolone with the aid of a two-stage system. In the first stage substance "S" is hydroxylated in the 11β-position with formation of cortisol by the mycelium of the fungal culture of *Curvulatia lunata* immobilised in a polyacrylamide gel and the cortisol is converted into prednisolone in the second stage in a column filled with immobilised steroid Δ^{1-2}-dehydrogenase from *Corynebacterium simplex*.

Workers in the German Democratic Republic devised an enzyme electrode based on cytochrome P-450.[126,132] With its aid, it is possible to detect low concentrations of many substrates of cytochrome P-450 by following the consumption of hydrogen peroxide in the reaction with the aid of a sensor electrode.

The practical employment of hydroxylating enzyme systems involves the solution of several complex problems, since such systems consist of multienzyme complexes and require the use of cofactors. Cytochrome P-450 and other components of the system are unstable and expensive. It is therefore necessary to solve the following problems on the way to the practical utilisation of cytochrome P-450 containing monooxygenases:

(1) Simplification of the involved multienzyme complex by decreasing the number of its components and by replacing biomolecules which are difficult to isolate by simpler and more readily available analogues;

(2) stabilisation of cytochrome P-450 by immobilising microsomes or isolated components of the hydroxylating complex[133-139];

(3) practical utilisation of simpler analogues of cytochrome P-450, which retain its function;

(4) immobilisation of micro-organism cells containing hydroxylating complexes[130,141,140].

One of the ways of solving the first problem was proposed by ourselves[29]: the complex electron transport chain of microsomes is replaced by organic hydroperoxides, whose combination with one component of the system (oxidised cytochrome P-450) effects all the reactions characteristic of the complete system. This simplification of the hydroxylating complex greatly decreases the cost of the catalytic system and makes it possible to reduce the involved task of immobilising the entire multienzyme complex to the immobilisation of one of its components—cytochrome P-450.

Further advances in the utilisation of hydroperoxide systems require a successful immobilisation of cytochrome P-450 and its stabilisation with respect to the second component—the organic hydroperoxide. In many laboratories attempts have been made to immobilise cytochrome P-450 from liver microsomes and other natural sources[127,129,133-139] In all cases cytochrome P-450 partly retained its activity, but, after several hours or days, the activity of the immobilised haemoprotein decreases significantly. The task of increasing the stability of the immobilised cytochrome P-450 and of simplifying its immobilisation therefore still remains urgent. It is known that the stability of certain enzymes can be significantly increased by their immobilisation not directly on a matrix but via binding it to an inert protein, which is then in its turn immobilised on a support. In particular such an inert protein may be serum albumin. Berezin and coworkers[142,143] showed that the immobilisation of peroxidase on BrCN-Sepharose, subjected to a preliminary modification with albumin, or the immobilisation of oligomers obtained by the interaction of peroxidase with albumin in the presence of glutaraldehyde leads to a significant stabilisation of peroxidase. The present author and his coworkers[136] immobilised highly purified cytochrome P-450 from rabbit liver microsomes on a modified albumin Biogel P-300 and investigated its activity in the hydroxylation of aniline by cumenyl hydroperoxide. This immobilisation method increases significantly the thermal stability of cytochrome P-450 and ensures the oxidation of aniline to *p*-aminophenol with kinetic characteristics close to those of the same reaction involving non-immobilised cytochrome P-450. After immobilising cytochrome P-450 by sorption on polyamide or nylon-6, specimens of a "dry" catalyst, retaining a high activity for 19 days, were obtained[138].

A detailed study of the degradation of cytochrome P-450 by hydroperoxides suggests that it can be prevented[45,144] by introducing radical reaction inhibitors into the system. The necessity to increase the thermal stability of cytochrome P-450 entails a complex problem. Systematic study of the thermal inactivation of cytochrome P-450 from rabbit liver showed that the stability of the haemoprotein increases significantly when 20% of glycerol is added to the solution and also for certain ways of immobilising cytochrome P-450.[145] According to the present author, further advances in the application of cytochrome P-450 will be achieved using certain new procedures for the stabilisation of enzymes developed by Berezin and Martinek[146,147]: by carrying out the reactions in two-phase "water–water-immiscible organic solvent" systems, by incorporating the enzyme in inverted surfactant micelles in organic solvents, etc.

The studies on the practical utilisation of the unique properties of cytochrome P-450 are only beginning. However, certain advances have already been achieved in this field, but their number is still small. There is no doubt that enzyme reactors and selective oxidation processes will be devised on the basis of cytochrome P-450 and its analogues.

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Copper Salts in Catalytic Reactions of Organic Compounds

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The reactions of copper complexes and organocopper compounds are examined and described systematically. Attention is concentrated on the reactions of copper complexes leading to the formation of carbon-carbon bonds. The influence of various parameters on the mode and mechanism of cuprocatalytic reactions is discussed.
The bibliography includes 343 references.

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I. INTRODUCTION

The study of catalytic processes involving unsaturated systems and the search for ways of their practical utilisation constitute one of the most rapidly developing fields of organic chemistry. Syntheses using catalysts based on copper salts or organocopper compounds are very common[1-12]. By virtue of their unusual and to some extent unique catalytic properties, copper salts have long attracted the attention of many investigators; thus copper(I) chloride is used as the catalyst in numerous important industrial processes—the synthesis of vinylacetylene, acrylonitrile, vinyl chloride, acetaldehyde, etc.

In assessing the reactions occurring in the presence of organocopper catalysts, one may say that they continue to serve as some of the fundamental synthetic methods in modern organic chemistry whereby one can obtain compounds of various classes[8,9,13]. Despite the fact that the first reaction involving organocopper compounds was achieved as early as 1869 by Glaser, the chemistry of these reactions has undergone particular development in the last two decades. Thus, up to the 60's of the present century, only six reactions based on organocopper compounds [reactions (1)–(6)] were known[13-18].

A. Substitution reactions

1. Symmetric oxidative coupling reactions:
(a) the Glaser reaction[15,16]:

$$2RC{\equiv}CCu \xrightarrow{\text{oxidation}} RC{\equiv}CC{\equiv}CR\ ; \quad (1)$$

$$2N{\equiv}CCu \xrightarrow{\text{oxidation}} N{\equiv}CC{\equiv}N\ ; \quad (2)$$

(b) the Ullmann synthesis of biaryls[15,17]:

$$2Ar{-}X \rightarrow Ar{-}Ar\ . \quad (3)$$

2. Asymmetric oxidative coupling reactions:
(a) the Rosenmund synthesis of nitriles[15]:

$$N{\equiv}CCu \xrightarrow{N_2^+Ar} N{\equiv}CAr\ ; \quad (4)$$

(b) the Gattermann synthesis of nitriles[15]

$$N{\equiv}CCu \xrightarrow{N_2^+Ar} NCAr\ . \quad (5)$$

B. Addition reactions

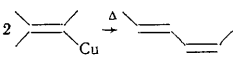
The Straus reactions[18]:

$$RC{\equiv}CCu \xrightarrow{HC{\equiv}CR} RC{\equiv}CCH{=}CHR\ . \quad (6)$$

In the course of the last twenty years a further six new reactions [reactions (7)–(12)] were discovered on their basis[4,5-28].

A. Substitution reactions

1. Symmetrical oxidative coupling reactions:
(a) reactions of vinyl derivatives of organocopper compounds[19-22]:



(7)

(b) oxidative coupling of copper *at*-complexes[23]:

$$[Alk{-}Cu{-}Alk]^-Li^+ \xrightarrow{\text{oxidation}} Alk{-}Alk\ . \quad (8)$$

2. Asymmetric oxidative coupling reactions:
(a) reactions of copper acetylides with aryl halides[5,6,24,25]:

$$RC{\equiv}CCu \xrightarrow{IAr} RC{\equiv}CAr\ ; \quad (9)$$

(b) synthesis of hydrocarbons from copper *at*-complexes and aryl halides[26]:

$$[CH_3CuCH_3]^-Li^+ \xrightarrow{IAr} CH_3Ar\ . \quad (10)$$

B. Addition reactions of copper *at*-complexes

(a) Addition to a double bond[27]:

$$[CH_3{-}Cu{-}CH_3]^-Li^+ \xrightarrow{\overset{CO-}{=}} CH_3{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{-}CO{-}\ ; \quad (11)$$

(b) addition to a triple bond[28]:

$$[CH_3{-}Cu{-}CH_3]^-Li^+ \xrightarrow{\overset{CO_2CH_3}{=}} \diagdown\!\!=\!\!\diagup_{CO_2CH_3}\ . \quad (12)$$

If we add to the above the fact that organocopper compounds catalyse also the coupling of organomagnesium compounds with various halides[29,30] or the dimerisation of alkyl, alkenyl, or alkynyl groups[29-32] starting with Grignard complexes

$$R{-}MgX \rightarrow R{-}R$$

as well as the use of complex copper salts as oxidants, (Benedict's, Barfoed's, Fehling's, Pavy's, etc. reagents)[33], etc., then the wide spectrum of the action of organocopper complexes and organocopper compounds in organic chemistry will become clear.

Simultaneously with the vigorous research into cuprocatalysis, elegantly written reviews have appeared in recent years in the literature[8-14,17], whose authors discuss mainly the reactions of homo- and hetero-cuprates and devote less attention to the reactions proceedings via organocopper complexes[34-36]. In order to survey the available literature data on numerous reactions with organocopper compounds and copper complexes, in the present review an attempt was therefore made to give a systematic account of the extensive experimental data on reactions involving organocopper complexes; attention is concentrated on the catalytic reactions of unsaturated compounds in the presence of copper salts.

Among organocopper compounds, one usually distinguishes homocuprates, heterocuprates, and copper π-complexes with organic compounds. However, the reactions of copper complexes and cuprates, particularly heterocuprates, are frequently difficult to distinguish from the reactions of pure organocopper compounds. Following the example of many investigators who have already surveyed various aspects of the reactions of organocopper compounds, we shall also consider these reactions together for the sake of convenience and when dictated by necessity.

II. ADDITION REACTIONS

1. Halogenation

A hydrochloric acid solution of copper chlories is an effective chlorinating agent whereby acetylene can be converted into *trans*-dichloroethylene[37-48]. Similarly a mixture of copper(I) and copper(II) bromides brominates acetylene to dibromoethylene[42]. It has been reported[43] that the chlorination reaction also yields 1,1-dichloroethylene[43]. According to certain data, when the chlorination[49,50] as well as the bromination[51] reaction is carried out in less acid media and in the presence of an excess of copper salts, tri- and tetrahalogenoethylenes are formed[49,50,52]:

$$HC{\equiv}CH \rightarrow HCX{=}CX_2\ ;$$
$$HC{\equiv}CH \rightarrow CX_2{=}CX_2\ ;$$
$$X = Cl, \text{ or } Br.$$

Copper(II) halides convert cyanoacetylene almost quantitatively into dihalogenoacrylonitrile[53]:

$$HC{\equiv}CCN \rightarrow HCX{=}CXCN\ ;$$
$$X = Cl \text{ or } Br.$$

A mixture of copper(I) and copper(II) salts was subsequently widely used in the halogenation of vinylacetylene[38,44,54], phenylacetylene[44], diacetylene[54,55], divinylacetylenes[56], as well as acetylenic[57-61] and diacetylenic[62,63] compounds with functional groups. It is remarkable that only the triple bond is then halogenated:

$$RC{\equiv}CH \rightarrow RCX{=}CXH\ .$$

Various workers have frequently dealt with the problem of the elucidation of the mechanism of the halogenation of multiple bonds[3,4,39,57,64-69]; attempts were made to provide an experimental basis for and to relate all the processes occurring in cuprocatalytic solutions[3,4,57,65,70]. However, at present it is impossible to give an exhaustive answer to numerous questions arising in the discussion of the mechanism of these reactions.

The halogenation of acetylene and its derivatives is usually carried out in aqueous or aqueous alcoholic solutions; dimethylformamide (DMF), dioxan, etc. are also used as solvents. However, under analogous conditions alkenes or alkadienes do not interact with bivalent copper salts. Thus it has been shown that the chlorination of butadiene can be achieved only with the aid of copper chloride melts[71-73] or in a fluidised catalyst bed[74]. In all the instances indicated the main reaction products were 3,4-dichlorobut-1-ene and a mixture of *cis*- and *trans*-1,4-dichlorobut-2-enes:

$$CH_2{=}CHCH{=}CH_2 \rightarrow \begin{cases} \rightarrow ClCH_2CH(Cl)CH{=}CH_2 \\ \rightarrow ClCH_2CH{=}CHCH_2Cl\ . \end{cases}$$

Subsequently it proved possible to halogenate various diolefins by adding various ligands and reducing agents[75-79]. Among these processes, the reaction in which butadiene is converted into a mixture of 1- and 2-chlorobutadienes is of particular interest[75]:

$$CH_2{=}CHCH{=}CH_2 \rightarrow \begin{cases} \rightarrow CH_2{=}CClCH{=}CH_2 \\ \rightarrow ClCH{=}CHCH{=}CH_2\ . \end{cases}$$

Finally, one should note that copper(II) chloride has also been used to halogenate alkenes and cycloalkenes[61]. As was to be expected, this reaction is less successful than for alkynes.

2. Hydrohalogenation and Addition of Hydrocyanic Acid

One of the most important fields of application of copper salts involves their use as catalysts of the hydrohalogenation of acetylene[80] and vinylacetylene[81]:

$$HC{\equiv}CH \xrightarrow{HX} CH_2{=}CHX\ ;$$
$$H_2C{=}CHC{\equiv}CH \xrightarrow{HX} CH_2{=}\underset{X}{C}{=}CHCH_2X \rightarrow$$
$$\rightarrow CH_2{=}\underset{|}{C}CH{=}CH_2\ .$$

Vinyl chloride and chloroprene continue to be synthesised in many countries on the basis of these reactions. Various alkynes, alkenynes, and their derivatives also enter into this reaction. Studies in this field have been frequently discussed and surveyed by various workers[81-83].

It has been found[84] that the triple bond activated by complex copper salts combines with hydrogen cyanide:

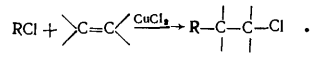
$$RC{\equiv}CH \xrightarrow{HCN} RHC{=}CHCN\ .$$

This method is still one of the most acceptable procedures for the synthesis of acrylonitrile, which is an extremely important monomer and reagent in organic chemistry.

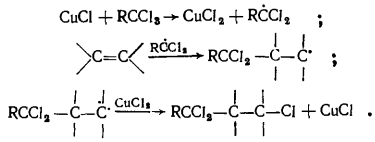
3. The Asscher–Vofsi Addition

Another important application of copper salts involves their use as catalysts of the alkylation of unsaturated systems by organic polyhalogeno-compounds. Thus Asscher and Vofsi[85-87] showed that, in the presence of copper ions, chloroform,

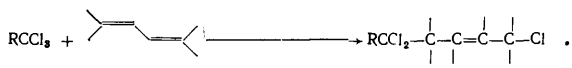
carbon tetrachloride, bromotrichloromethane, and sulphonyl chloride add smoothly to alkenes:



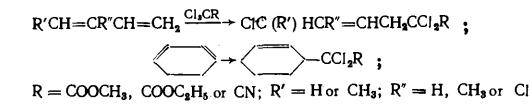
It is of interest that under these conditions a copper(I) salt is an effective catalyst of the chloroalkylation of olefins[88,89], the radical being regenerated via the following mechanism in its presence:



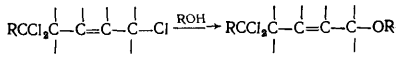
Analogous results have been obtained by other workers in the reaction of alkenes and styrene, on the one hand, and carbon tetrachloride, trichloroacetonitrile, and dichloroacetonitrile, on the other[90-92]. Copper(I) salts have been used successfully also for the halogenoalkylation of various dienes with chloroform, carbon tetrachloride, and bromotrichloromethane[85,88,93]:



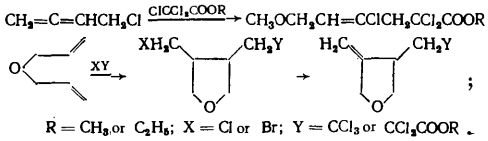
From the preparative point of view, together with the reaction described above, the alkylation of butadiene, isoprene, piperylene, cyclohexadiene, chloroprene, and other halogenodienes with trichloroacetate esters and trichloroacetonitrile in the presence of copper(I) oxide is of considerable interest[94-97]:



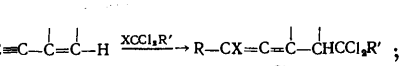
It is remarkable that, when the reaction is carried out in protic solvents, copper(I) salts promote the solvolysis of the allylic halogen generated in the process with formation of an ether[95,96]:



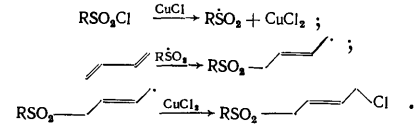
This catalyst has been used successfully for the addition of polyhalogeno-derivatives of organic compounds to cumulated and isolated dienes[94,98]:



It has been shown recently that copper(I) oxide is an effective catalyst of the addition of bromotrichloromethane, trichloroacetate esters, and trichloroacetonitrile to vinyl-, isopropenyl-, and cyclohexenyl-acetylenes and their functional derivatives and satisfactory yields of various allene derivatives have been obtained[94,97,98]:



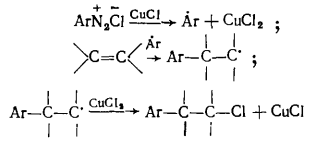
The interaction of various sulphonyl chlorides with dienes also takes place successfully in the presence of copper salts[88,100-103]. The occurrence of the reaction via the following mechanism is usually postulated:



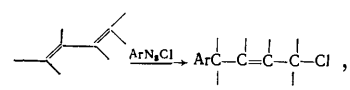
The chlorides of organic sulphonic acids add smoothly under analogous conditions, i.e. in the presence of copper(II) chloride, to vinylacetylenic hydrocarbons[104,105], as well as their silicon-substituted analogues[106,107]. It has been shown that, in the case of hydrocarbons with the normal structure of the enyne residue, the addition is to the double bond whereas in the case of the silicon-containing analogues 1,4-addition is also observed. Thus the Asscher–Vofsi reaction makes it possible to synthesise various organoelemental compounds from ethylene, acetylene, and their derivatives.

4. The Meerwein Arylation

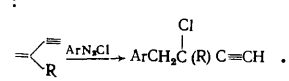
Copper(I) salts have been used successfully in the arylation of alkenes and their derivatives by diazonium chlorides via the Meerwein reaction[108-110]:



Various dienes[109,111], alkynes, enynes[109,112,113] also undergo the Meerwein arylation. Interesting features of the coupled addition of the aryl residue and the halogen to dienes and particularly to enyne systems have been discovered. In the first place one should mention the ability of diazonium salts to arylate conjugated dienes in the 1,4-positions[109,111,113]:



and also the arylation of conjugated enyne compounds at the double bond[81,82,114]:



The characteristics of the reaction associated with the influence of neighbouring groups in unsaturated systems, the presence of substituents in the aromatic ring of diazonium salts, the pH of the medium, the nature of the solvents, the role of the catalyst, etc. are likewise noteworthy and exhaustive information about them can be obtained from elegantly written reviews of the Meerwein reaction[108,109]. It is remarkable that various polyfunctional compounds which are difficult to obtain by othe procedures have been synthesised by the above reaction.

5. The Reppe–Jones Alkynol Synthesis

It has been established that the complex catalyst based on copper salts is effective in the condensation of acetylene with formaldehyde not only under pressure[115-124] but also

without it[124-132]:

$$HC{\equiv}CH \rightarrow HOCH_2C{\equiv}CCH_2OH \ .$$

The reaction takes place more successfully with other aldehydes[115] and with terminal vinylacetylenes[133].

It has been reported quite recently that copper(II) ions catalyse effectively the aldol condensation reaction[134,135]:

$$ArCHO \xrightarrow[Cu^{2+}]{R'CH_2COR} ArCH{=}\overset{R'}{\underset{|}{C}}{-}COR \ .$$

6. Generation of Carbenes

Among cuprocatalytic reactions, the application of complex catalysts based on copper salts in the generation of carbenes is of considerable interest. The characteristic features of the behaviour of the carbenes, obtained in the presence of copper ions, in addition reactions, rearrangements, etc. have been investigated[136-140].

III. SUBSTITUTION REACTIONS

Copper salts have found extensive applications as successful catalysts also in substitution reactions.

1. Solvolytic Reactions

It has been shown[141] that the hydrolysis of allyl chloride is accelerated when a hydrochloric acid solution of copper hemichloride is added to the reaction medium. On the basis of kinetic studies, the authors[141] concluded that the rate of hydrolysis is determined by the stage involving the ionisation of allyl chloride bound in a complex:

$$CuCl + Cl^- \rightarrow \widetilde{CuCl_2} \ ;$$
$$CH_2{=}CHCH_2Cl + CuCl_2^- \rightarrow [CH_2{=}CHCH_2Cl \cdot CuCl_2]^- \ ;$$
$$[CH_2{=}CHCH_2Cl \cdot CuCl_2]^- \rightarrow [CH_2{=}CHCH_2 \cdot CuCl_2] + Cl^- \ ;$$
$$[CH_2{=}CHCH_2CuCl_2] + \overline{OH} \rightarrow CH_2{=}CHCH_2OH + \widetilde{CuCl_2} \ .$$

Continuing the study of the solvolysis of substituted allyl halides in relation to individual stereoisomers, the same workers concluded that the $CuCl_2^-$ ions behave as the catalyst in these reactions[142-144]. The catalytic effect of copper salts on the hydrolysis of allyl chloride in an alkaline medium has also been confirmed in another study[145].

It is noteworthy that another group of investigators demonstrated the possibility, in principle, of the catalysis by copper salts of the reverse reaction, i.e. the formation of allyl chloride from allyl alcohol[146-148]:

$$CH_2{=}CHCH_2OH \xrightarrow[CuCl]{HCl} CH_2{=}CHCH_2Cl \ .$$

2. The Exchange of a Halogen

It has been established recently that copper(I) and copper(II) salts catalyse the exchange of the halogen in allyl halides[149-151]:

$$RR'C{=}CHCH_2Cl \xrightarrow[Cu^+/Cu^{2+}]{HX} RR'C{=}CHCH_2X \ ;$$
$$X = Cl \text{ or } Br.$$

It is of interest that in the case of substituted allyl halides the migration of the reaction centre is observed simultaneously[150]:

$$CH_2{=}CHCCl_3 \rightarrow BrCH_2CH{=}CCl_2 \ ;$$
$$CH_2{=}CHC(Cl)RR' \rightarrow RR'C{=}CHCH_2Br \ .$$

3. Mixed Reactions

Certain examples available at the present time in the literature show that substitution of the allyl chlorine[152] or hydroxyl[153] by a weak nucleophile such as the cyanide ion can also be successfully catalysed by a copper halide:

$$ClCH_2CH{=}CHCH_2Cl \xrightarrow[Cu^{2+}]{KCN} NCCH_2CH{=}CHCH_2CN \xrightarrow[Cu^{2+}]{HCN} HOCH_2CH{=}CHCH_2OH \ .$$

It is striking that, when crotyl chloride is involved in the reaction, dehydrocondensation via the hydrogen atoms of the methyl group takes place simultaneously[154].

Copper salts are likewise effective catalysts of the interaction of the allylic halogen with ammonia and primary and secondary amines[155]:

$$CH_2{=}CHCH_2Cl \xrightarrow[Cu^+/Cu^{2+}]{HNRR'} CH_2{=}CHCH_2NRR' \ ;$$
$$R = H \text{ or Alk}; \ R' = Alk \ .$$

According to patent data[156], copper or its salts can be used as catalysts for the synthesis of unsaturated amines via the mechanism

$$ClCH_2CH(Cl)CH_2Cl \xrightarrow{H_2NR} CH_2{=}C(Cl)CH_2NHR \ .$$

Polyhalogenoalkenes have also been made to react with amines in the presence of copper(II) salts[157]. There have been a number of reports concerning the application of copper(II) salts as catalysts in the reaction of aryl halides with ammonia or amines, leading to the formation of aniline derivatives[158-163].

4. Substitution of the Hydrogen in C–H Acids

(a) For a halogen. According to the available literature data, copper salts promote both the substitution of hydrogen by a halogen in alkanes, aldehydes, and ketones and the dehydrohalogenation of halogenoalkanes[164-173]. They have been used successfully for the synthesis of α-halogenoalkynes from terminal acetylenic compounds[61,174] and for the chlorination of butadienyl sulphone to 1,1,4,4-tetrachlorobuta-1,3-diene.[175]

(b) For dialkylamino-groups. It is also well known that copper salts catalyse the Mannich reaction, in particular the substitution of active acetylenic hydrogen for a dialkylamino-group[176,177]:

$$R{-}C{\equiv}CH \xrightarrow{R'CHO,\ HNR'R''} R{-}C{\equiv}C{-}C(R')HNR'R'' \ .$$

5. The Sandmeyer Reaction

The conversion of diazonium compounds into aryl halides by the substitution of diazo-groups by chlorine via the Sandmeyer reaction, where copper(I) salts are again used as catalysts, can serve as an interesting example of cuprocatalysis[178]. According to Kochi[179], the reaction can be represented schematically as follows:

$$ArN_2Cl \xrightarrow{CuCl} \overset{+}{ArN_2}Cu\overline{Cl_2} \ ;$$
$$\overset{+}{ArN_2}Cu\overline{Cl_2} \rightarrow \dot{A}r + CuCl_2 + N_2 \ ;$$
$$\dot{A}r \xrightarrow{CuCl_2} ArCl + CuCl \ .$$

IV. ALKYLATION, ARYLATION, AND ACYLATION

1. The Colonge–Korts Alkylation

Copper(I) salts are used as catalysts of the alkylation of terminal acetylenes with allyl halides[180–188]:

$$RC{\equiv}CH \xrightarrow{XCH_2C(R'''){=}CR'R''} RC{\equiv}CCH_2C(R'''){=}CR'R''.$$

Allylacetylenes, allylacetylenic alcohols, etc. have been synthesised in this way. A catalytic amount of copper(I) chloride is usually sufficient for the reaction. It is striking that under analogous conditions propargyl chlorides react mainly with inversion of the reaction centre[189,190]:

$$RC{\equiv}CH \xrightarrow{ClCH_2C{\equiv}CH} RC{\equiv}CCH{=}C{=}CH_2 .$$

We may note that allenyl halides with the halogen at an sp^2-hybridised carbon atom enter into this reaction[191]:

$$RC{\equiv}CH \xrightarrow{ClCH{=}C{=}CR'R''} RC{\equiv}CCH{=}C{=}CR'R'' .$$

The alkylation of cyanoacetic ester by propargyl halides in the presence of zerovalent and univalent copper are closely related to the above reaction[192]:

$$HC{\equiv}C{-}\underset{Cl}{\underset{|}{C}}RR' \xrightarrow{NCCH_2CO_2C_2H_5} HC{\equiv}CC(RR')\underset{CN}{\underset{|}{C}}HCO_2C_2H_5 .$$

Finally copper(I) oxide has been used successfully for the alkylation of allylisonitrile with allyl bromide via the mechanism[193]

$$CH_2{=}CHCH_2NC \xrightarrow{BrCH_2CH{=}CH_2} \begin{cases} \rightarrow CH_2{=}CHCH(\underset{CN}{\underset{|}{}})CH_2CH{=}CH_2 \\ \rightarrow CH_3CH(\underset{CN}{\underset{|}{}})C{-}CH_2CH{=}CH_2 \end{cases} .$$

2. The Sladkov–Castro Arylation, Alkylation, and Acylation

The arylation of ethynylcopper compounds by aryl halides constitutes yet another important field of application of organocopper compounds[5,6,24,25,186,194–197]:

$$RC{\equiv}CCu + ArX \rightarrow RC{\equiv}C{-}Ar ;$$

R = Ar, furyl, etc.; X = I or Br.

Subsequently this method was extended to many classes of organic compounds. Studies in this field have been examined systematically and in detail by Sladkov, Ukhin, and Gol'ding[5,6].

Copper acetylides are smoothly alkenylated by compounds containing an allylic halogen atom[198–200]:

$$RC{\equiv}CCu + XCH_2C(R'){=}CR''R''' \rightarrow RC{\equiv}CCH_2C(R'){=}CR''R''' .$$

Studies by a number of workers have shown that vinyl halides are also capable of reacting with copper acetylides[189, 200,201]; furthermore, the involvement of α-halogenoketones in the above reaction made it possible to develop a fairly convenient method of synthesis of furan derivatives[200]:

$$PhCOCH_2Br \xrightarrow{CuC{\equiv}CR} Ph{-}\underset{O}{\langle\!\rangle}{-}R .$$

The Sladkov–Castro reaction has also been used successfully to synthesise important natural products, particularly pheromones[202]. The reaction of copper acetylides with acid halides shown below is also of interest[199,203]:

$$RC{\equiv}CCu \xrightarrow{R'C(=O)Cl} RC{\equiv}CCOR' .$$

V. REARRANGEMENTS

1. Allyl Halides

The very wide variety of the catalytic properties of copper(I) and copper(II) salts has led to the possibility of using them in the anionotropic rearrangements of unsaturated systems. Such rearrangements are usually characteristic of allyl and propargyl halides. As an illustration, one may quote the isomerisation of 1,4-dichlorobut-2-ene to 1,2-dichlorobut-3-ene in the presence of copper halides on heating[204,205]:

$$ClCH_2CH{=}CHCH_2Cl \rightarrow ClCH_2CH(Cl)CH{=}CH_2 .$$

According to other data[206], 1,4-dichlorobut-2-ene is converted into 1,1-dichlorobut-3-ene under the influence of copper or copper(I) oxide:

$$ClCH_2CH{=}CHCH_2Cl \rightarrow Cl_2CHCH{=}CH_2 .$$

In recent years the synthesis of chloroprene from butadiene has assumed great practical importance. This largely accounts for the attempts by a number of workers to elucidate the possibility of the interconversion of the butadiene chlorination products and to establish their configuration. It was found[207] that, in the presence of copper(I) salts at 35° to 90 °C, an equilibrium mixture of *cis*-1,4-dichlorobut-2-ene (5–6%), *trans*-1,4-dichlorobut-2-ene (70–80%), and 1,2-dichlorobut-3-ene (15–20%) is obtained. Next it was shown that 1,4-dichlorobut-2-ene readily isomerises to 1,2-dichlorobut-3-ene on refluxing in the presence of $CuCl_2$:[208]

$$ClCH_2CH{=}CHCH_2Cl \rightarrow CH_2{=}\underset{Cl}{\underset{|}{C}}HCH_2Cl .$$

One should note particularly that copper naphthenates[209,210] and acetylacetonate[211] have been used as catalysts for the anionotropic isomerisation of allylic halides:

$$CH_3\underset{Cl}{\underset{|}{C}}HCH{=}CH_2 \rightarrow CH_3CH{=}CHCH_2Cl .$$

Cuprocatalysis also occurs in the conversion of 4-chlorobuta-1,2-diene into chloroprene[212]:

$$ClCH_2CH{=}C{=}CH_2 \rightarrow CH_2{=}CClCH{=}CH_2 .$$

2. Propargyl Halides

The conversion of dichlorbutyne into a diene dihalide in the presence of copper(I) chloride and ethylamine hydrochloride in DMF is of great interest[213]:

$$ClCH_2C{\equiv}CCH_2Cl \rightarrow CH_2{=}CClCCl{=}CH_2 .$$

It is known that propargyl halides isomerise to halogenoallenes under the influence of copper(I) salts[214,215]:

$$RR'C(\underset{X}{\underset{|}{}}){-}C{\equiv}CH \rightarrow RR'C{=}C{=}CHX ;$$

X = Cl or Br.

When copper salts were used in reactions involving substitution of a hydroxyl for hydrogen in hydrogen halide solutions it was found that, together with acetylenic halides, halogenoallenes are also obtained[216,217]:

$$RR'C(\underset{OH}{\underset{|}{}}){-}C{\equiv}CR'' \rightarrow RR'CC{\equiv}CR + RR'C(\underset{X}{\underset{|}{}}){=}C{=}CR'' .$$

A comprehensive study of this reaction showed that allenic compounds are products of the isomerisation of acetylenic halides catalysed by copper salts[216,217]:

$$RR'C(X)-C\equiv CR'' \rightarrow RR'C=C(X)=CR''$$

Studies in this field have been surveyed in reviews by Vartanyan and Badanyan[216], Wotiz[217], and others[218-220], in which the available extensive literature data on this field are examined in detail and described systematically.

3. Rearrangements of Other Systems

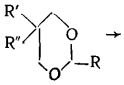
It has been established that copper-based catalysts are used successfully for the rearrangement of α,β-unsaturated alcohols to aldehydes and ketones[221,222]. Here it is important that the latter are formed via the hydrogenation of the intermediate α,β-unsaturated carbinols:

$$RCH=CH-CH(OH)R' \rightarrow RCH=CHCOR' \rightarrow RCH_2CH_2COR' .$$

More detailed data on the anisotropic transformations of alkenes and alkynes can be found in a collection of articles[223] and in a review[218].

In many instances copper complexes are used for prototropic isomerisations[224,225], *cis–trans* transformations[225], the Wolff rearrangement[227], the synthesis of polycyclic compounds[228], the disproportionation of substituted benzenes[229], and for other purposes[230].

Finally one should note the rearrangement of *m*-dioxans to β-alkoxyaldehydes in the presence of copper–silver catalysts[231]:



$$\rightarrow ROCH_2C(R'R'')CHO .$$

VI. DIMERISATION REACTIONS

1. Oxidative Dimerisation

(a) The Glaser and Cadiot–Chodkiewicz oxidative dimerisation of acetylenes. Oxidative coupling reactions of various acetylenes in the presence of copper(I) salts are known in the chemical literature. Here in the first place mention should be made of the Glaser reaction[232] and its modification by Eglinton[238] and also the Cadiot–Chodkiewicz method[234,235] whereby asymmetrically substituted diacetylenes can be obtained.

Recently studies in this field have been surveyed by Eglinton and McCrae[236,237] and other workers[238,239]. The applications of the above reactions and the influence of various factors on the yield and direction of the process are examined and the pathways via which they occur are discussed in these reviews.

(b) Dimerisation of other C–H acids. It has been found[240] that, in the presence of copper(I) salts in pyridine, phenyl-substituted acetonitriles are converted by atmospheric oxygen or various peroxide compounds into adiponitrile derivatives[240]. Ketonitriles behave similarly[241,242]. Studies on the oxidative coupling of other C–H acids (arenes, aryl halides, thiophen and its derivatives, etc.) via organocopper compounds with formation of a carbon–carbon bond have been widely developed and have been the subject of a special discussion[13,14].

The catalytic properties of copper salts have been used successfully by a number of investigators for the oxidative polymerisation of aromatic hydrocarbons[243,246]. Copper salts can be used for the oxidative dehydrodimerisation of hydrogen cyanide[247]:

$$N\equiv CH \rightarrow N\equiv C-C\equiv N .$$

It is remarkable that copper(I) and copper(II) oxides as well as various copper(II) salts catalyse the dimerisation–addition of α,β-unsaturated carbonyl compounds—nitriles, esters, and ketones[248-252]:

$$R'CH=CHR- \begin{cases} \rightarrow R'CH=C(R)C(R')HCH_2R \\ \xrightarrow{R'=H} RCH_2CH=CHCH_2R \\ \xrightarrow{CH_2=CHR} R'CH=C(R)CH_2CH_2R \end{cases} ;$$

R = COAlk, COOAlk or CN .

The above reaction is regarded[248-252] as a special type of the Michael addition. A good example of the dehydrocondensation is also the dimerisation of acrylonitrile in the presence of copper(II) ions, which leads to the nitrile of hexenedicarboxylic acid[253]:

$$2CH_2=CHCN \rightarrow NCCH_2CH=CHCH_2CN .$$

(c) Dimerisation of organometallic compounds. The cuprocatalytic dimerisation reactions of Grignard reagents with alkyl halides, which made it possible not only to increase the rate of coupling of the alkyl residues of the above class of compounds but also to apply the method successfully to other syntheses, proved to be particularly productive. Studies in this field have been surveyed by Tamura and Kochi[254]. Analogous question have been partly dealt with in the reviews of Schlosser[255], Posner[11,12], and Normant[8], who considered the problems of the formation of a C–C bond with the aid of organometallic reagents. Another important method of synthesis of various hydrocarbons is the coupling reaction of alkyl, alkenyl, and alkynyl derivatives of lithium, magnesium, zinc, and aluminium, as well as other organometallic compounds in the presence of copper salts[11-14,17,254-257].

2. The Straus–Neuland Dimerisation of Acetylenes

Straus showed that the copper derivative of phenylacetylene dimerises to 1,4-diphenylbut-3-ene-1-yne on heating with acetic acid[258]:

$$C_6H_5C\equiv CCu \rightarrow C_6H_5C\equiv CCH=CHC_6H_5 .$$

Subsequently other workers extended the above reaction to various terminal acetylenes[259-261]. However, the most important result of these studies was the finding that an acid medium promotes the dimerisation of acetylenes, as a result of which cuprocatalytic methods were successfully applied to the dimerisation of acetylene and its monosubstituted homologues to vinylacetylene and its derivatives[2,3,4,80,81,262]:

$$2RC\equiv CH \rightarrow RCH=CHC\equiv CR .$$

The process is usually carried out in a hydrochloric acid solution of copper(I) chloride and is still used in the manufacture of chloroprene from acetylene[80,81,263].

3. Reductive Dehalogenodimerisation Reactions

(a) The Ullmann dehalogenodimerisation of aryl halides. The Ullmann reaction, which consists in the reaction of aryl halides with powdered copper at a high temperature, has

already been widely used for the synthesis of a wide variety of aromatic systems in the course of several decades[264,265]:

$$Ar{-}X \xrightarrow{Cu} Ar{-}Ar + CuX_2 \ .$$

The available literature data on this reaction have been frequently described in reviews[264,265], in which the present limits of the applicability of the reaction, its conditions, and the influence of various substituents and the solvent, as well as the question of the application of a series of copper compounds [copper(I) oxide and copper(I) and copper(II) salts] as additives or independent catalysts are clearly defined; the kinetics of the reaction have been examined in detail and its probable mechanisms have been put forward.

It is appropriate to mention that metallic copper or copper salts in various oxidation states are used successfully also in the so called Ullmann condensation, i.e. in the reaction of aryl halides with anilines[265]:

$$ArCl \xrightarrow{Ar'\text{-}NH_2} ArNHAr' \ .$$

In their studies of the influence of various added copper(I) and copper(II) salts on the Ullmann condensation, some workers[266,267] concluded that copper(I) ions are the catalytically active form for this reaction and that the application of bivalent copper must be accompanied by reducing agents[268].

(b) The dehalogenodimerisation of α-halogenoethers and allyl, propargyl, and benzyl halides. There has been a recent growth of interest in the so-called dehalogenodimerisation reactions of organic halogeno-compounds, which occur in the presence of zerovalent or univalent copper. One of the first reports on this field[269] showed that, on refluxing with metallic copper, various α-chloroethers are converted into ethylene glycol derivatives in high yields:

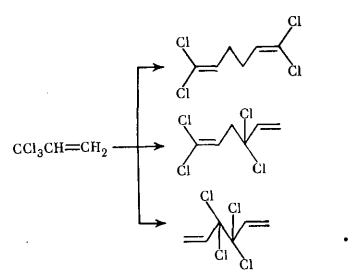
$$RCOCH_2Cl \rightarrow ROCH_2CH_2OR$$
$$R = CH_3,\ ClCH_2CH_2 - \text{etc.}$$

A little later data were published on the dehalogenodimerisation of allyl halides. Thus Yagupol'skii and Chaika[270] showed that trichloromethylalkenes give rise to chloro-substituted bisallyls and trienes in pyridine in the presence of copper via the mechanism

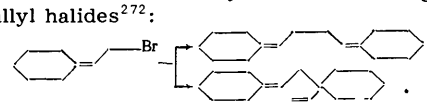
$$RCH{=}CHCCl_3 \rightarrow RCH{=}CHCCl_2CCl_2CH{=}CHR \rightarrow RCH{=}CHCCl{=}CClCH{=}CHR$$
$$R = H,\ C_6H_5,\ COOH,\ COOCH_3 \text{ or } COC_6H_5 \ .$$

It was established that the yield of trienes greatly increases when the reaction is carried out in acetonitrile.

In a somewhat later study it was reported that, in the presence of copper powder in pyridine, trichloromethylethylene dehalogenodimerises to a mixture of all the expected hexadienes[271].



It is of interest that the organocopper complexes obtained from alkyl-lithium and copper iodide in the presence of dialkylamines are effective catalysts of the dehalogenodimerisation of allyl halides[272]:



The results showed that the dehalogenodimerisation reaction is specific only to compounds containing a mobile halogen atom. A study by Japanese workers on the dehalogenodimerisation of allyl and benzyl halides[273,274] provides a good illustration of this postulate. It was observed that both allyl and benzyl chlorides give rise to high yields of dimers in the presence of the copper(I) cation in ethylenediamine, diethylenetetramine, triethylenetetramine, acetylacetone, and ethylenediaminetetra-acetic acid (EDTA):

$$\overset{I}{CuCl} + n\,(en) \rightarrow \overset{I}{Cu}\,(en)_nCl \ ;$$
$$RCH_2Cl + 2\overset{I}{Cu}\,(en)_nCl \rightarrow RCH_2CH_2R + 2\overset{II}{Cu}\,(en)_nCl_2 \ .$$

The replacement of the above solvents by ethanolamine, pyridine, bipyridyl, phenanthroline, or triphenylphosphine suppresses the reaction.

In the presence of the above catalysts [$Cu^I(en)_nCl$] benzyl chloride derivatives (trichloromethylbenzyl, dichlorodiphenylmethane, and chlorodiphenylmethane) behave similarly, with the sole difference that the resulting chloroethanes are then converted into stilbenes[275,276]:

$$C_6H_5C\,(R)\,Cl_2 \rightarrow C_6H_5\overset{R}{\underset{|}{C}}Cl{-}\overset{R}{\underset{|}{C}}ClC_6H_5 \rightarrow C_6H_5\overset{R}{\underset{|}{C}}{=}\overset{R}{\underset{|}{C}}C_6H_5 \ ;$$
$$(C_6H_5)_2C\,(R)\,Cl \rightarrow (C_6H_5)_2\overset{R}{\underset{|}{C}}{-}\overset{R}{\underset{|}{C}}\,(C_6H_5)_2 \xrightarrow{R=Cl} (C_6H_5)_2C{=}C\,(C_6H_5)_2 \ .$$

We may note that this reaction is also catalysed by iron(II) salts.

The available literature data show that the dehalogenation of halogenoalkanes in the presence of both copper salts[276] and zerovalent copper[278-284] is accompanied by partial dehalogenodimerisation with formation of halogenoalkene derivatives.

We believe that, among all the existing ideas concerning the mechanism of the dehalogenodimerisation of allyl systems[271,274], the most likely is the view of Hashimoto and coworkers[274], according to which all these reactions can be interpreted as oxidation-reduction processes via the mechanisms:

$$\overset{I}{Cu} + n\,(en) \rightarrow \overset{I}{Cu}\,(en)_n \ ;$$
$$RCH_2Cl \xrightarrow{\overset{I}{Cu(en)_n}} RCH_2CH_2R + \overset{II}{CuCl_2} \ ,$$

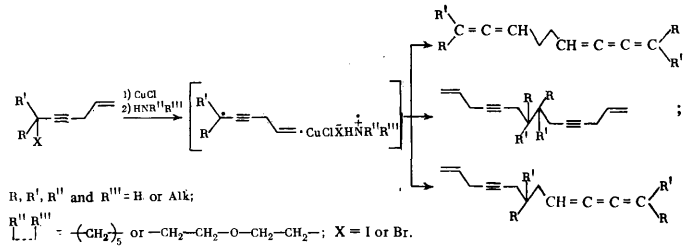
or

$$2RCH_2Cl \xrightarrow{\overset{I}{CuCl}} 2\,[RCH_2Cl \ldots CuCl \leftrightarrow R\dot{C}H_2\overset{II}{Cl}\overset{I}{Cu}Cl] \rightarrow RCH_2CH_2R + \overset{II}{CuCl_2} \ ,$$

or

$$RCH_2Cl \xrightarrow{\overset{I}{CuCl}} RCH_2ClCuCl \xrightarrow{\overset{I}{CuCl}} RCH_2\overset{I}{Cu}Cl + CuCl_2 \ ;$$
$$2RCH_2\overset{I}{Cu}Cl \rightarrow RCH_2CH_2R + 2\overset{I}{CuCl} \ .$$

Badanyan showed recently that vinylpropargyl halides are converted into a mixture of unsaturated hydrocarbons in the presence of copper(I) salts and amines (primary or secondary) via dehalogenodimerisation[285-295]. The authors believe that the process proceeds via the mechanism



It was shown that complexes of copper salts with amines containing hydrogen attached to the nitrogen atom exhibit a catalytic activity, the yield of product depending greatly on the ionisation potential of the amines[288,293,295].

The study of the influence of substituents in various positions in the system revealed certain regularities. Thus it has been found that an increase in the bulk of the alkyl groups at the carbon atom attached to the halogen in vinylpropargyl halides not only decreases the overall yield of hydrocarbons but also increases the fraction of anomalous dehalogenodimerisation products—unsaturated hydrocarbons with cumulated multiple bonds[286,288,295].

An interesting picture was observed when vinylpropargyl halides with substituents at the double bond were introduced into the reaction. Thus in the case of vicinal substitution (at the double bond) of the halides, the yield of the anomalous dehalogenodimerisation products increases; in contrast, geminally substituted or trisubstituted unsaturated halides give rise only to dienediyne hydrocarbons[290,291]:

$$RR'C(X)C{\equiv}CC(CH_3){=}CHR'' \rightarrow HC(R'){=}C(CH_3)C{\equiv}CC(RR')C(RR')C{\equiv}CC(CH_3){=}CHR'';$$

R, R′, and R″ = H or alkyl.

The different types of behaviour of the systems investigated can be readily accounted for within the framework of the electronic effects of the substituents and the steric hindrance generated by them. In the study of the effect of the medium and also of various additives on this reaction, it was concluded[293,295] that the reaction proceeds via the formation of radical intermediates. Here it is important that, when a reducing agent (hydroxylamine hydrochloride), is introduced into the reaction medium, the reaction becomes catalytic[295].

It is noteworthy that, under the conditions of the dehalogenodimerisation of vinylpropargyl halides, allyl chlorides containing electron-accepting substituents also enter into this reaction[292]:

$$RR'C{=}C(R'')CH_2Cl \rightarrow RR'C{=}C(R'')CH_2CH_2C(R''){=}CRR'';$$
R, R′ and R″ = H or Cl.

There are literature data concerning the reductive dimerisation of ethers of acetylenic carbinols[296], allenic halides[297], and other systems[298] catalysed by copper or its salts.

It has been reported that in the presence of metallic copper trichloromethylbenzene dehalogenodimerises to dichlorostilbene[299]:

$$C_6H_5CCl_3 \rightarrow C_6H_5CCl{=}CClC_6H_5.$$

The dehalogenodimerisation of α-halogenoacids[300]

$$RR'CBrCOOR'' \rightarrow RR'C(COOR'')-CRR'(COOR'')$$

and of acid chlorides[301]

$$RCOCl \rightarrow RCOCOR$$

is of interest from the practical point of view.

Finally one should note that the amine complexes of copper(I) salts catalyse the intramolecular cyclisation of propargyl ethers[302].

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It is evident from the above that during recent years definite advances have been made in the field of cuprocatalytic reactions on the basis of which methods of synthesis of many types of organic compounds have been developed. These processes are undoubtedly still of enormous interest, as shown by the vigorous present development of homogeneous cuprocatalysis based on isonitrile complexes of copper and its salts. The above catalysts are used widely for the synthesis of derivatives of cyclopropane, cyclobutane, cyclopentane, oxazoline, oxazine, imidazoline, thiazole, pyrroline, etc. Earlier data on this field have been surveyed[303]. Synthetic studies on these lines are being continued[304-312]. It is remarkable that copper complexes of the above type catalyse the insertion of isonitriles in the heteroatom—hydrogen bond in amines[311,313,314], alcohols[308,315,316], thiols[317,318], phosphines[319], and silanes[330] and also the esterification of alkanoic, halogenoalkanoic, and halogenoarenoic acids and their anhydrides[321-323]. Isonitrile complexes of copper are used in the binding of carbon dioxide[324-329] and in prototropic[314] and *cis–trans*[323,330] isomerisations. It is extremely important that they catalyse the Michael, Tishchenko, Meerwein–Ponndorf, and analogous reactions[251,330-338], the dimerisation of α,β-unsaturated nitriles and carbonyl compounds[248,249,330-332,339], and the polymerisation of alkenes and their derivatives[340-343]. There is no doubt about the prospects for the further development of both the theoretical and practical aspects of cuprocatalytic reactions; a more profound understanding of their essential features and their control are the tasks for the immediate future.

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Advances in the Chemistry of Isoindole

F.S.Babichev, V.A.Kovtunenko, and A.K.Tyltin

Data on the synthesis and physical and chemical properties of isoindoles published in 1968-1978 are examined and problems of the aromaticity of *o*-quinonoid heterocycles (isobenzofuran, isothionaphthene, and isoindole) are discussed. The bibliography includes 214 references.

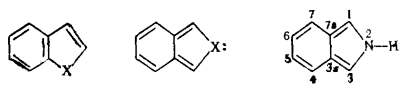
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I. INTRODUCTION

The annelation of benzene and aromatic five-membered heterocycles containing one heteroatom (pyrrole, furan, and thiophen) leads to two classes of bicyclic compounds isoelectronic with naphthalene. If the annelation takes place along the *b* side, the products are the so-called normal isomers or, according to recent chemical usage, type (I) Kekulé isomers: indole (X = NH), benzofuran (X = O), and thionaphthene (X = S). Annelation along side *c* of the five-membered ring leads to isomeric *o*-quinonoid heterocycles of type (II): isoindole (III), isobenzofuran (X = O), and isothionaphthene (X = S). These two classes of heterocycles exhibit fundamental differences of their electronic structure and properties.

Heterocycles of type (I) have been known for more than 100 years and comprise thoroughly investigated stable compounds. Their type (II) isomers have been obtained only comparatively recently after numerous unsuccessful attempts; they proved to be extremely reactive. Among these compounds, isoindole is particularly interesting.



(I) (II) (III)

Since the publication of the first review[1] on the isoindole chemistry, more than 10 years have elapsed. During this period, the parent compound (III) has been synthesised, new methods have been developed for the synthesis of isoindoles, their chemical properties have been investigated in detail, and practical applications have been found for isoindole derivatives. Certain new data on individual aspects of the isoindole chemistry have been described in reviews[2,3], but the information concerning isoindoles in monographs on the chemistry of benzopyrroles[4-7] does not go beyond the information contained in the review of White and Mann[1].

This survey includes all studies on the chemistry of isoindole mentioned in Chemical Abstracts during the last 10 years. It does not deal with condensed isoindoles, tetrahydroisoindoles, isoindolines, and also compounds of type (IV) (X = RC); Svirevski's review is devoted to compounds of the last type[8].

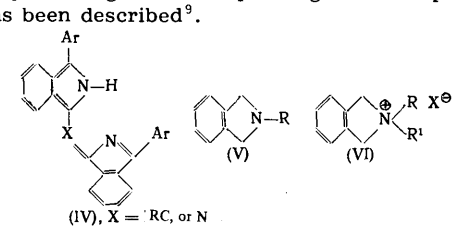
II. METHODS OF SYNTHESIS OF ISOINDOLES

1. Synthesis of Isoindoles from Isoindolines

Two ways of converting isoindolines (V) into isoindoles are possible: (a) the elimination method and (b) the oxidation method. In view of the lack of thoroughly developed methods for the single-stage mild oxidation of compounds (V), the elimination method is preferable.

(a) The Elimination Method

The Wittig method, which consists in treating quaternary ammonium salts (VI) (R = R^1 = alkyl) with strong bases, is not nowadays widely used. Only the synthesis of 2-methylisoindole by treating the corresponding salt with phenyllithium has been described[9].



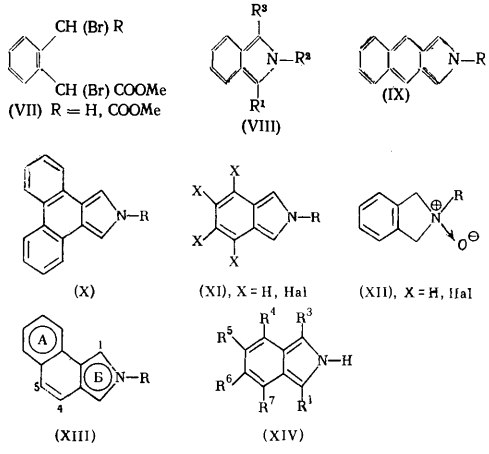
(IV), X = RC, or N (V) (VI)

A method has been proposed recently[10] for the synthesis of 2-substituted isoindoles from hydrazinium salts (VI, R^1 = NHR^2) by treatment with an excess of alkali or a base; compound (V, R = $BuOOCNCH_2CH{=}CH_2$) and not 2-allylisoindole is formed from the salt (VI, R = $CH_2CH = CH_2$, R^1 = NHCOOBu) under these conditions. The initial salts (VI, R^1 = NHR^2) need not necessarily be isolated in a pure state from the reaction mixture in their synthesis from 1,2-bis(bromomethyl)benzenes and hydrazines[10]. Large series of 1,2,3-trialkylisoindoles have been synthesised by this method[14].

It has been shown that isoindoles are formed in a single stage from the esters (VII) with R = H[12,13] and R = COOMe[11,12] and the corresponding hydrazines with subsequent elimination of ammonia from the intermediate salt of type (VI). It was impossible to make hydrazine hydrate react with the dibromo-derivatives (VII) and obtain isoindoles (VIII, R^2 = H). The interaction of compound (VII) with phenylhydrazine is more complex, but in this case too it is possible to isolate the isoindoles (VIII, R^2 = Ph).[13] Isoindoles (IX) and (X)

with R = Me have been synthesised by the same method from 2,3-bis(bromomethyl)naphthalene and 9,10-bis(bromomethyl)-phenanthrene[15].

Isoindoles (XI, R = alkyl, X = Br) have been obtained in high yields by the acetolysis of the amine oxides (XII) on treatment with a mixture of acetic anhydride and triethylamine[16]. A somewhat different method has been used[17] to synthesise isoindoles (XI, X = H). For the mechanism of the acetolysis of amine oxides, see von Volz and Ruchti[18]. Pyrolysis of amine oxides (XII) is also used to obtain isoindoles[19,20].



Benzoisoindoles (X, R = H)[22] and (XIII, R = H)[23] have been obtained by treating substituted 2-tosylisoindolines with strong bases. It has been shown[24-26,177] that isoindoles (XIV) can be synthesised successfully from 2-methanesulphonyliso-indolines, which are treated with an excess of potassium t-butoxide in DMSO[21-25,28] or of sodionaphthalene[22] in dimethoxyethane (XXII).

The parent isoindole (III) was first obtained by Bonnett et al.[20,27] in 1972 by the pyrolysis of isoindoline (V, R = OCOOMe). Thermal decomposition of the same isoindoline in a solvent also gives rise to isoindole, which has been demonstrated by the formation of an adduct with *N*-phenylmaleimide[20]. The formation of isoindole from 2-hydroxyisoindoline when the latter is treated with acetic anhydride is indicated by the isolation of the same adduct[20].

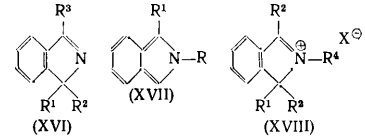
(b) The Oxidation Method

The method involving the direct single-stage oxidation of *N*-substituted isoindolines (V) for the synthesis of the corresponding isoindoles began to develop only recently. It has been shown[17] that the self-oxidation of 2-butyliso-indoline depends on the nature of the solvent and is a free-radical process. 1,3-Dimethoxycarbonylisoindole and *N*-alkyl derivatives have been obtained by oxidising the corresponding isoindolines at room temperature with atmospheric oxygen. 1,3-Disubstituted isoindolines having the *cis*-configuration are oxidised to isoindoles much more readily than their *trans*-isomers[21].

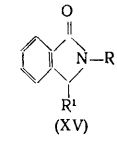
2-Arylisoindolines are entirely stable in air at the usual and elevated temperatures and other oxidants must be used to obtain isoindoles from them[21]. Thus the oxidation of compounds (V, R = Ar) to the corresponding isoindoles can be achieved with the aid of chloranil in high-boiling solvents. A heterolytic reaction mechanism, initiated by hydride transfer, is then postulated[29]. The aromatisation of isoindolines using chloranil has been used to synthesise a number of isoindoles (VIII) and gave various yields (23–80%)[13]. The use of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and the synthesis of 4- and 5-azaisoindoles from the corresponding azaisoindolines have been described[30].

2. Syntheses of Isoindoles via Phthalimidines

Phthalimidines (XV) are structurally similar to isoindoles. Judging from ^{1}H NMR spectra[21], they do not show a tendency towards formation of one of the possible tautomeric lactim forms (XVI, R^3 = OH) or (XVII, R^1 = OH), but Wittig showed[1] that they can be successfully converted into isoindoles either by treatment with organolithium compounds or by reduction. Isoindoles (VIII) are formed in high yields when phthalimidines are treated with a solution of methyllithium[14,32]. 2-, 3-, and 6-Substituted phthalimidines have been used as starting materials in the reaction with methyllithium.



Together with methyl-lithium, ethyl-, butyl-, or vinyl-lithium can be employed in this reaction[14].



Previously Wittig obtained 2-methyl- and 2-phenyl-isoindoles by treating the corresponding phthalimidines with $LiAlH_4$ in ether and subsequent pyrolysis of the intermediate lithium alkoxide. In the case of 2-benzylphthalimidine the corresponding isoindole could not be obtained. The replacement of $LiAlH_4$ by sodium bis(2-methoxyethoxy)aluminium hydride (SBMAH)[33] gives a 60% yield of 2-benzylisoindole. In addition it has been found that the same isoindole can be obtained from *N*-benzylphthalimidine when the latter is treated with SBMAH, while the use of $LiAlH_4$ gives rise solely to the isoindoline (V, R = CH_2Ph).[33]

A new method of synthesising isoindole derivatives involving the use of the Vilsmeier reagent has been developed recently[34,35]. When phthalimidines (XV, R^1 = H) are treated with twice the amount of dimethylformamide (DMF) and $POCl_3$, the salt (XVIII, $R^1 + R^2 = CHNMe_2$, R^3 = Cl) is formed and on heating with alkali is converted into the isoindole (VIII, R^1 = Cl, R^3 = CHO). Treatment of the salts (XVIII, $R^1 + R^2 = CHNMe_2$, R^3 = Cl or Br, R^4 = H) with bases gives rise to the isoindolenine (XVI, $R^1 + R^2 = CHNMe_2$, R^3 = Cl or Br), which can also be converted in its turn into an isoindole of type (XIV)[34]. If the substrate : reactant ratio is altered to equivalent proportions, the reaction product is tris(1-oxoisoindolino)methane. The use of Vilsmeier reagents for the synthesis of azaisoindoles has also been described[36,171].

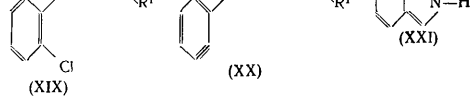
When phthalimidines (XV, R = H) were treated with cyclic immonium salts (formed on mixing pyridine, quinoline, or isoquinoline with benzoyl chloride), isoindoles (VIII) containing the residues of these heterocycles in the 1- and 3-positions were obtained[37]. Phthalimidines (XV), where $R^1 = CH_2Ar$ and R = H, can be aromatised in a similar manner. The reaction of cyclic immonium salts with phthalimidines is one of the examples of the heterylation reaction, the mechanism of which has been described[38].

The lactim forms (XVI, $R^3 = OH$) and (XVII, $R^1 = OH$) can be stabilised by their *O*-alkylation. This reaction has been known for a long time, but interest in 1-alkoxyisoindolenines has increased recently in connection with their use in the synthesis of various nitrogen-containing isoindole derivatives[39-42]. The *O*-alkylation of phthalimidines takes place at room temperature on mixing solutions of phthalimidine and trialkyloxonium fluoroborates in inert solvents. The resulting salts (XVIII, $R^3 = OR$) are converted into 1-alkoxyisoindoles on treatment with strong bases[39-42]. The reaction of Meerwein reagents with 2-methyl- and 2-ethyl-phthalimidines also takes place smoothly, but with formation of salts giving rise to isoindoles (XVII, $R^1 = OAlk$) on treatment with bases[43].

The formation of aza-derivatives of isoindole (XVII, $R^1 = OAlk$) has been described[171].

3. Syntheses of Isoindoles via *o*-Disubstituted Benzenes

Heterocyclisation processes involving dehydrobenzene are known[44], but, when molecules with a potential aryne functional group (for example, a chlorine atom in an aromatic ring) have a side chain exhibiting nucleophilic properties [as in *o*-chlorobenzylamines (XIX)], then intramolecular cyclisation is possible at an intermediate stage in the generation of the aryne (XX). An example of such heterocyclisation is provided by the elegant synthesis of 2-methylisoindole from the amine (XIX, R = H, $R^1 = CN$) and potassium amide in liquid ammonia (89%)[44,45]. Isoindoles (XVII, R = Me, $R^1 = COOR^2$, $CONH_2$, or COPh) have also been obtained by this procedure in very low yields. The mechanism of the reaction (XIX) → (XVII) is still not altogether clear[46].

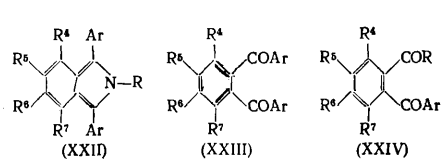


A very simple method of synthesising aminoisoindole (XXI, $R = NH_2$) from the dinitrile of phthalic acid by reduction with $LiAlH_4$ has been proposed[47,48]. The same isoindole can be obtained by the catalytic hydrogenation of *o*-azidomethylbenzonitrile[56].

Babichev and Tyltin[49,55] found that the reaction of *o*-chloromethylbenzonitrile on heating with amines produces in a single stage derivatives of aminoisoindole (XVII, $R^1 = NH_2$) and not benzylamine derivatives, as claimed previously[50], and not 2-substituted phthalimidines, as described in patents[51,183]. A series of similar compounds have also been obtained in other studies[52-54,57] as a result of the interaction of *o*-chloro(bromo)methylbenzonitriles with various primary amines. The corresponding bis-compounds have been obtained from *m*- and *p*-phenylenediamines[55].

Phthalonitrile and its substituted derivatives react with organomagnesium compounds to form red-violet compounds with structure (XIV, X = N); the isoindoles (XVI, R^1 + R^2 = NH) are intermediates in this reaction[58].

1,3-Diphenylisoindoles (XXII) can be obtained by condensing *o*-diacylbenzenes (XXIII) with primary amines or ammonium acetate[59,60].



This method[1], devised by Emmet, was developed further in other investigations[61-66]. The process can be regarded as a modified Leuckart reaction; when applied to compounds (XXIV), it leads to low yields of isoindoles[1,67]. In order to increase the yield, it has been suggested[63] that an alcoholic solution of methylamine be used and that sodium tetrahydroborate be added to the reaction mixture. A number of biologically active isoindoles have been obtained from the benzophenones (XXIV, R = COOEt or $CONR_2^1$)[65,66] on treatment with diethylaminoethylammonium formate.

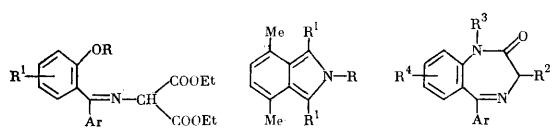
Maekawa and coworkers investigated the reaction of *o*-acylbenzophenones with ammonia[61,62] and primary amines[64,117]. Whereas the interaction of compound (XXIV, R = Ar) with ammonium formate leads to isoindoles, as shown above, the reaction of compound (XXIV, R = Me or Et) under these conditions results in the formation of low yields of isoindole self-condensation products—stable dark-blue pigments (IV, X = RC). Depending on the conditions, three types of compounds can be obtained in the reaction of compound (XXIV, R = Me) with primary alkylamines[64,117].

It follows from the study of Do Minh et al.[68] that none of the products of the interaction of *o*-phthalic aldehyde with ammonia and amines is an isoindole. On the other hand, a mixture of *o*-phthalic aldehyde and β-mercaptoethanol is a familiar and widely used biochemical reagent for the spectofluorimetric determination of aminoacids and proteins[69]. Simons and Johnson[70] suggested that the fluorescent products of the reaction of the above reagent with the *N*-terminal groups of aminoacids and proteins are isoindoles (XVII, $R^1 = SAlk$). To test this hypothesis, *o*-phthalic aldehyde was condensed with n-propylamine in the presence of ethanethiol, β-mercaptoethanol[70], t-butanethiol[71], thiophenol[72], and other thiols. Isoindoles have been isolated in the pure form only in the case of t-butanethiol and ethanedithiol. The formation of isoindoles (XVII, $R^1 = SAlk$) in alcoholic solutions has been investigated[72] by ultraviolet spectroscopy and NMR. The condensation products exhibit a strong fluorescence, which in general confirms the above hypothesis.

It has been shown[73] that, when *o*-acetylphenylacetic acid is condensed with hydroxylamine, the isoindole (XIV, R^1 = Me, R^3 = COOH) is formed in a high yield. A novel method of synthesising isoindoles has been described in a patent[74]. On heating with a large excess of imidazole (or alkylimidazoles), compounds (XXV) give rise to isoindoles (XIV, R^1 = Ar, R^3 = COOEt) in 16–60% yields; in the absence of imidazoles, the reaction does not take place.

On condensation with 1,2-dicyano- or 1,2-dibenzoylethanes, 3,4-diformyl-1,2,5-trimethylpyrrole gives rise to 5,6-dicyano(dibenzoyl)-1,2,3-trimethylisoindoles[75]. Derivatives of 5-aza- and 5,6-diaza-isoindoles have also been obtained from this pyrrole[75].

4. Condensation of 1,4-Diketones with Amines or Pyrroles

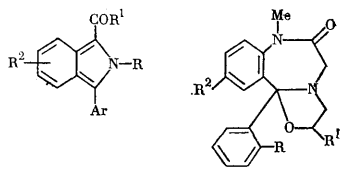


If both α-positions of the pyrrole ring are occupied, as, for example, in 2,5-dimethylpyrrole, then condensation with 1,4-diketones results in the formation of isoindole derivatives (XXVI)[1]. When a mixture of 1-R-2,5-diphenylpyrrole[19] or 1-R-2,5-dimethylpyrrole[19,28,76] and hexane-2,5-dione is refluxed in acetic acid, the corresponding isoindoles (XXVI)

are formed. The isoindole (XXVI, R = Me) was obtained in a single stage from methylamine and hexane-2,5-dione[19,76]. It was shown[28] that refluxing of a solution of 2,5-dimethylpyrrole in aqueous acetic acid results in the formation of the isoindole (XXVI, R = H) in 82% yield as a result of self condensation. This finding is of interest, because it had been observed earlier[1] under similar conditions that 2,5-dimethylpyrrole undergoes reductive self condensation with formation of a mixture of *cis*- and *trans*-1,3,4,7-tetramethylisoindolines.

5. Isoindoles as Products of the Isomerisation of 1,4-Benzodiazepinones

The rearrangement of 1,4-benzodiazepinones to isoindoles, noted by White and Mann[1], has been used to obtain several series of biologically active isoindoles[65,66,77]. Thus 1,4-benzodiazepinones (XXVII) give rise to a high yield of the amides (XVIIIa, R = H) on treatment with NaH in DMF[65,66,77]. A rearrangement of the above type also takes place with thioanalogues of compounds (XXVII), which gives rise to high yields of thioamides[77].



(XXVIII) (XXIX)

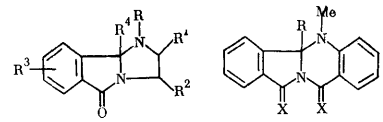
(a) R^1 = NHMe; (b) R^1 = OR^3

It has been shown[65,66] that, if the isomerisation is carried out in the presence of carbonic acid esters, then, instead of amides, the products are the esters (XXVIIb). A method of carrying out the single-stage transformation (XXVII) → (XXVIIIb, $R^3 = CH_2CH_2NEt_2$) has been described in a patent[65].

Like 1,4-benzodiazepin-2-ones, the esters (XXVII, R^2 = COOR) can be converted into isoindoles; the products are the isoindoles (XXVIIIb, R = H). An interesting difference in the behaviour of condensed benzodiazepinones (XXIX) under the conditions of isomerisation to isoindoles has been discovered[78]. It was found that compound (XXIX, R = Cl) isomerises to the corresponding isoindole, while compound (XXIX, R = H) gives rise to other products.

6. Reduction of Condensed Isoindoles with $LiAlH_4$

According to Sulkowski et al.,[80] treatment of imidazoisoindoles (XXX) with $LiAlH_4$ in diethyl ether yields 2,5-benzodiazocines. However, it has been shown[81-85,178] that, in the presence of an excess of $LiAlH_4$ and after prolonged refluxing of the reaction mixture, 2-(*N*-alkylaminoethyl)isoindoles are formed together with the corresponding diazocines. Under identical conditions, pyrimidoisoindoles are reduced by $LiAlH_4$ to 2-(aminopropyl)isoindoles[81,83,84] with high yields, while 1-methyl-1,3,4,10*b*-tetrahydro-2*H*-pyrimido[2,1-*a*]isoindol-6-one is reduced to the isoindole [XVII, R = $(CH_2)_3NHMe$].[86] The reduction of the benzo-analogue (XXX, R = R^3 = H) with an excess of $LiAlH_4$, followed by treatment with alcohol, gives rise to the isoindole (XVII, R = 2′-$C_6H_4NH_2$).[83]



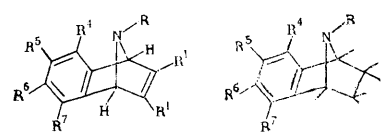
(XXX) (XXXI)

A pattern, which is similar in broad outline, is observed in the reduction of compounds of type (XXXI, X = O) with $LiAlH_4$. The reduction product is compound (XXXI, X = H_2) which isomerises during chromatography to the isoindole (XVII, R = 2′-$CH_2C_6H_4NHMe$).[83,87]

7. Synthesis of Isoindoles by the Diels–Alder Retro-Reaction

The study of the Diels–Alder retro-reactions, taking into account their similarity with mass-spectrometric, thermal, and photochemical processes, contributed much new information to the chemistry of simple isoindoles and isobenzofurans and yielded extremely useful results[88]. The first data on the thermal decomposition of derivatives of 7-azabenzonorbornadiene (XXXII) were obtained as early as 1963 by Wittig[89], who isolated α-naphthylamine in the thermolysis of the hydrobromide of compound (XXXII, R = R^{4-7} = H). In 1966 Carpino and Barr[90] obtained similar results.

The first evidence for the possibility of obtaining isoindoles from compounds (XXXII) was obtained by Coe and Uff[91]. Subsequently it was found that the loss of ethylene in the mass-spectra of 7-azanorbornenes (XXXIII) constitutes the principal type of fragmentation of the molecular ion (XXXIII, R = Me, R^{4-7} = F), and the isoindole (XI, R = Me, X = F) was isolated quantitatively in the thermolysis of the above compound at a temperature as low as 120 °C.[88] The essential feature of the Diels–Alder reaction consists in the thermolysis of the products (XXXII) and (XXXIII) obtained initially by the Diels–Alder reaction. An example of the direct conversion of compound (XXXII, R = R^{4-7} = H) into isoindole with elimination of acetylene has been described[92,187].



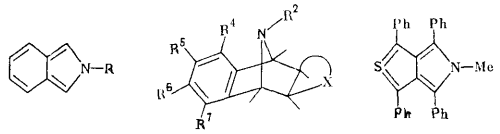
(XXXII) (XXXIII)

Thermolysis of derivatives of compound (XXXIII) leads to the loss of an ethylene molecule and the formation of the corresponding isoindole. The isoindoles obtained by the Diels–Alder retro-reaction are very pure. The isoindoles (XXIV)[93], (XI, R = H, Me, or CH_2Ph, X = F),[94,95] and benzo[*f*]isoindole[95,176] have been obtained by this method.

An interesting version of the Diels–Alder retro-reaction has been proposed in a study[96] where it was shown that the derivatives (XXXII) readily undergo the [2 + 4] cycloaddition reaction with 3,6-dipyridyl-*sym*-tetrazine to form the 1,1-adducts [XXXV, X = C(α–Py) = N–N = C(α–Py)], whose thermolysis gives rise to a mixture of isoindole and 3,6-di-α-pyridylpyridazine. This procedure was used by Anderson[97] to obtain isoindoles, but the adduct [XXXV, X = –NPh–N= C(Ph)–] then undergoes pyrolysis.

The synthesis of the isoindole (III) by the high-vacuum pyrolysis of compound (XXXIII, R = COOBu) has been described[98]. 1-Methyl- and 1,3-dimethyl-isoindoles have

been obtained by this method from the corresponding derivatives (XXXIII). It has been established in relation to the Diels–Alder retro-reaction for 7-azabenzonorbornene (XXXIII) and 7-azanaphtho[2,3]norbornene that the pyrolysis of both compounds at 125 °C leads exclusively to deamination (i.e. results in the formation of naphthalene and anthracene respectively); the relative yield of isoindole increases with increase of the pyrolysis temperature and reaches a maximum at 700–800 °C.[99]

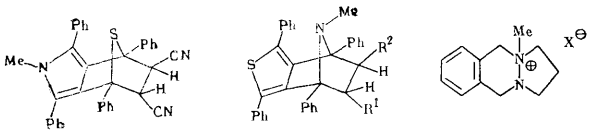


(XXXIV) (XXXV) (XXXVI)

The 1:1 adducts of the Diels–Alder reactions with condensed thiophens (XXXVI) are capable of giving rise to isoindoles under the conditions of the Diels–Alder retro-reaction[100,101]. Thus, when a mixture of equimolar amounts of compound (XXXVI) and fumaronitrile is refluxed in xylene for 12 h, the isoindole (XXII, $R^{4,7}$ = Ph, R = Me, $R^{5,6}$ = CN) is formed in 53% yield. On being refluxed in toluene for 12 h, fumaronitrile and compound (XXXVI) form compound (XXXVII) in 67% yield, while refluxing in benzene for 1 h gives a 63% yield of compound (XXXVIII). Both compound (XXXVII) and compound (XXXVIII) are capable of being converted into the above isoindole in a high yield on being refluxed in xylene. The adduct (XXXVII) can be converted into isoindole also on mixing its solution in methanol with sodium methoxide. The thienopyrrole (XXXVI) undergoes similar reactions with acrylonitrile and ethyl acrylate[100,101].

8. Synthesis of Isoindoles by the High-Vacuum Pyrolysis of Heterocyclic Compounds

High-vacuum pyrolysis—one of the modern methods of synthesising new heterocyclic systems[102]—has also been used to obtain isoindoles. Thus it has been shown[103] that isoindole derivatives can be obtained by the vacuum flash pyrolysis of phenyl-1,2,4-triazoles. The possible mechanism of the formation of isoindole in the thermolysis of triazoles includes the 1,5-sigmatropic shift of the *N*-phenyl group and the formation of a non-aromatic intermediate, the elimination of molecular nitrogen, and the cyclisation of the iminocarbene (or the 1,3-biradical) to 1,3-diphenylisoindole[103].



(XXXVII) (XXXVIII) (XXXIX)

The vacuum pyrolysis of *N*-(2-hydroxy-3-isoquinolinyl)-urethane at 600 °C affords 1-cyanoisoindole in quantitative yield[104,105,179]. It has been mentioned in patents[105,179] that this method can be used to synthesise also 1-cyanoisoindoles substituted in the benzene ring. The necessary condition is then the stability of the substituent on pyrolysis; the most suitable substituents proved to be the fluorine and chlorine atoms and the Me and CN groups[179].

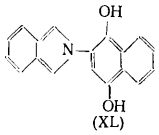
9. The Formation of Isoindoles in the Isomerisation of Heterocyclic Compounds

The rearrangement of 1-(4′-chlorophenyl)-2,5-benzodiazocine to derivatives of 2-aminoethylisoindole under the influence of strong bases is a familiar example[82,85]. The isomerisation is accompanied by the dehydrochlorination of the initial compound and, if there is no chlorine atom in the *p*-position in the benzene ring, which corresponds to the 1-position in benzodiazocine, then the product is 2-(β-aminoethyl)-1-phenylisoindoline[82].

A study of the reactions of isoquinoline derivatives with nucleophiles yielded interesting results for the chemistry of isoindole[106,107]. Thus it has been found that the amination of 3-amino-4-bromoisoquinoline with potassium amide in liquid ammonia gives rise to a mixture of 1-cyanoisoindole and 3-aminoisoquinoline[106]. The condensed hydrazinium salt (XXXIX) gives rise to 2-(3-methylaminopropyl)isoindole on treatment with potassium t-butoxide[86].

10. Other Methods of Synthesis of Isoindoles

When a benzene solution of *N*-(2-naphthoquinonyl)isoindoline is irradiated with light from a mercury lamp, an intramolecular oxidation–reduction reaction takes place with formation of the isoindole (XL).[108]



(XL)

Together with other products, the addition of di-t-butylthioketen to benzophenone methylimine results in the formation also of the isoindole (XVII, R = $CHPh_2$, R^1 = Ph).[109]

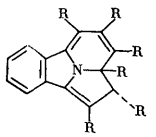
The oxidation of *N*-aminophthalimide produces phthalimidonitrene, while the reaction of the latter with isobenzofuran derivatives has been shown[110] to constitute a pathway leading to a high yield of 2-phthalimidoisoindole.

The two-electron polarographic reduction of 1,2-dihydrophthalazines in an acid medium initially produces isoindole and then isoindoline[111].

III. PHYSICAL PROPERTIES

1. Bond Orders and Lengths

There are no literature data on the X-ray diffraction analysis of isoindole derivatives. The geometrical parameters of compound (XLI), whose structural element is an isoindoline fragment, are known[112].



(XLI)

The bond orders and lengths in isoindole, 1-phenylisoindole[114], 2-phenylisoindole, 1,3-diphenylisoindole[114], benzo[*f*]isoindole[15,114], benzo[*e*]isoindole[114,115], and dibenzo[*e*,*g*]-isoindole[14,114] have been calculated by the SCF MO[15,113–115] and *ab initio*[116] methods. It has been noted[115] that the calculated bond lengths in benzo[*e*]isoindole (XIII, R = H) indicate an appreciable localisation of the bonds between the (A) and (B) ring systems (see Section II, 1a).

2. Distribution of π-Electron Density and Dipole Moments

The results of the calculations of the distribution of π-electron density in the isoindole molecule and the calculated dipole moments have been published (Table 1)[15,115,116,118-120]. Analysis of these data indicates unambiguously the order in the variation of the π-electron density in isoindole (III): $q_1^\pi > q_{3a}^\pi > q_5^\pi > q_4^\pi$. According to the above sequence in the variation of the π-electron density, assignments were made to the corresponding protons in the ^{1}H NMR spectrum of 2*H*-isoindole[27]. The calculations showed that the effective π-electronic charges on the carbon atoms of the pyrrole ring in 1-phenylisoindole are greater, as in benzo[*e*]isoindole (XIII, R = H), than on the remaining carbon atoms[114]. The following sequence in the distribution of π-electron density holds for compound (XIII): $q_3^\pi > q_1^\pi \gg q_5^\pi$.

Table 1. The distribution of electron density in isoindole (III).

q_1^π	q_2^π	q_{3a}^π	q_4^π	q_5^π	μ, D	Computational methods	Refs.
1.14	1.59	1.05	1.00	1.02	2.66	SCF CI P—P—P	[118]
1.1553	1.5380	1.0468	1.0107	1.0182	—	SCF P—P	[115]
1.108	1.626	1.049	1.010	1.020	—	SCF P—P—P	[15]
1.0909*	1.6615	1.0424	1.0069	1.0136	2.29	SCF P—P—P	*
1.1275			1.0115	1.0251		SCF P—P—P	[119]
1.0589	1.8066	1.0308	0.9983	1.0087	—	SCF Pople	[114]
1.1261	1.5525	1.0725	1.0017	1.0236	2.94	*ab initio* (GTO)	[116]
1.1336**	1.5243	1.0729	1.0027	1.0258	3.43	*ab initio* (GTO)	[116]
1.1043	1.6305	1.0586	1.0040	1.0177	2.20	*ab initio* (STO—3G)	[120]

* 2-Phenylisoindole. Calculation carried out by V.I.Minkin.
** 2-Methylisoindole.

The data on the distribution of π-electron density make it possible to attempt an approach to its quantitative estimation in the series of *o*-quinonoid heterocycles (II) and their isomers (I) on the basis of the concept of the excess π-electron density in heterocycles. According to Pozharskii[121], the average negative charge per carbon atom of the heterocyclic system can serve as a measure of the excess π-electron density. Thus, according to the results of calculations[114], the average effective π-electronic charges on all the carbon atoms of pyrrole, isoindole, indole, and carbazole are respectively −0.040, and −0.024, −0.015, and −0.008, while on the carbon atoms of the pyrrole ring in the above compounds they are −0.040, −0.044, −0.024, and −0.013 respectively. The above results indicate a higher excess π-electron density in isoindole compared with indole.

The same conclusion can be arrived at by comparing the distribution of π-electron densities in the above compounds, obtained from SCF MO[115,118] and *ab initio*[120] calculations. Comparison of the effective π-electronic charges on the carbon atoms of the pyrrole ring in the above benzopyrroles and the parent compound indicate a higher excess of π-electron density in isoindoles (III) even by a comparison with pyrrole. Similarly the results of calculation[114] permit the conclusion that the excess π-electron density in isobenzofuran (II, X = O) is greater than in benzofuran (I, X = O); the results of calculations of the distribution of π-electron density in compounds (II, X = NH, S, or O)[116] when the latter are examined from the standpoint of effective π-electronic charges of the carbon atoms indicate a comparatively greater excess of π-electron density in isoindoles (III) compared with the remaining *o*-quinonoid heterocycles.

3. The Reactivity Indices of Isoindoles

Qualitative conclusions concerning the direction of electrophilic and nucleophilic attack as well as addition reactions have been reached on the basis of the calculated charge densities within the framework of the isolated molecule approximation[115]. The 1(3)-position in *o*-quinonoid heterocycles (II) is most likely to undergo electrophilic attack, while the 4(7)-position is most favourable for nucleophilic attack. Analysis of the bond orders of *o*-quinonoid heterocycles (II) led to the conclusion that the $C_{(4)}-C_{(5)}$ (or $C_{(6)}-C_{(7)}$) bond should be most reactive in addition reactions[115]. The calculated free valence indices of the above compounds made it possible to determine the preferential direction of attack in free-radical reactions; for all the *o*-quinonoid heterocycles, these are the $C_{(1)}-C_{(3)}$ atoms. According to Klasinc et al.,[115] in benzo[*e*]isoindole the $C_{(4)}$ atom is subjected to electrophilic attack, while nucleophilic and radical attack is directed to the $C_{(3)}$ atom. It is noteworthy that these conclusions[115] are inconsistent with the results of the determinations and calculations of the electron density in the molecule of compound (XIII).[114]

4. The NMR Spectra of Isoindoles

The first calculation of the chemical shifts of isoindoles (III) was carried out by Black et al.[122] With the aid of a modified VESCF method, the authors calculated the delocalised contribution (the contribution of ring currents) to the diamagnetic anisotropy $\Delta\chi$ of heteroaromatic molecules.

Heterocycle	$-10^6\,\Delta\chi$
Indolisine	39.39 — 39.58
Isoindole	43.76 — 44.94
Indole	45.12 — 45.83
Isobenzofuran	40.68 — 41.78

Calculation of the chemical shifts of the isoindole protons[122] led to the following sequence: $\delta_{4,7\text{-H}} > \delta_{1,3\text{-H}} > \delta_{5,6\text{-H}}$. Later the same sequence was established experimentally.[20,27,93] Recently attempts have been made to relate the ring current data to the degree of aromaticity of the entire molecule itself. Corradi et al.[119] calculated the contributions of the ring currents to the shielding constants. The results of the calculations support the idea of a limited degree of aromaticity of the above compounds. The conversion of the five-membered heterocycles into their benzo-derivatives results in an increase of the ring current effects relative to the sum of the currents of the individual constituent rings. The annelation of the benzene ring to the *b* side of the five-membered heterocycle [the Kekulé structure (I)] has been shown by calculation[119] to entail a greater delocalisation of electrons than the annelation to the *c* side [the *o*-quinonoid heterocycle (II)].[119]

Analysis of the ^{1}H NMR spectra of substituted isoindoles showed that, following the absorption of resonance energy by the protons, the following sequence obtains: $\delta_{4,7\text{-H}} > \delta_{1,3\text{-H}} > \delta_{5,6\text{-H}}$, although it can break down in certain cases for $\delta_{1,3\text{-H}}$, depending on the nature of the substitution in the system. For the chemical shifts of the protons of the methyl groups in 2*H*-isoindole derivatives, it is more difficult to observe a similar rule; however, the relation $\delta_{1,3\text{-Me}} > \delta_{4,7\text{-Me}}$ holds at least in many instances.

The ^{1}H NMR spectrum of the parent isoindole (III) has been obtained quite recently[20,27,93]. The four-spin system of the AA'BB' spectrum, corresponding to the spin—spin interaction of the protons in isoindole, has been analysed[15,116,123,125] with the aid of the LAOCN3[123-125], LAOCOONII[15],

LAMS[116], and NMRIT[125] programmes. In the first stage of the computations based on the LAMS programme calculations were made for the four-spin system AA'BB' (protons in the 4-, 5-, 6-, and 7-positions) and then for the six-spin system of the AA'BB'XX' spectrum (i.e. for additional H in the 1- and 3-positions). In order to determine the accurate spin–spin interaction constants (SSIC) of isoindoles, the results of the calculation were compared with experiment. The SSIC of isoindoles are compiled in Table 2. The ^{19}F NMR spectrum of 4,5,6,7-tetrafluoroisoindole has been recorded[97].

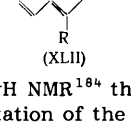
Table 2. The spin–spin interaction constants (SSIC) (J_{H-H}, Hz) of isoindoles.

Isoindole	$J_{4,5}=J_{6-7}$	J_{5-6}	$J_{4-6}=J_{5-7}$	J_{4-7}	Refs.
(III)	8.49	6.29	0.89	0.98	[123, 124]
(XXXIV) (R=Me)	8.60	6.28	0.86	0.98	[15]
ditto	8.690	6.456	0.899	0.790*	[116]
(VIII) (R^1=R^3=Ph, R^2=Me)	8.63	6.35	0.98	1.02	[15, 125]

* In addition, the transannular constants $J_{1-4} = 0.457$, $J_{1-6} = -0.070$, $J_{1-7} = -0.081$, and $J_{1-5} = 0.070$ are presented.

Data have been published[116,188] on the ^{13}C NMR spectrum of 2-methylisoindole. The similarity of the resonance absorption of energy by different carbon atoms is striking. The most characteristic feature of the 2-methylisoindole spectrum is the overall upfield shift of the absorption due to the carbocyclic ring carbon atoms (by ~ 6 p.p.m.); an even greater shift is observed for the $C_{(1)}$, $C_{(3)}$ atoms of isoindole, particularly in relation to the corresponding $C_{(2)}$ atoms of pyrrole or indole.

The ^1H NMR method combined with the shift reagent method [Eu(DPM)$_3$][126] made it possible to determine the structure of the preferred conformer of acyl derivatives of the isoindole (XLII, R = COR^1, R^1 = H or Me). In both cases the phenyl substituent in the 2-position is displaced from the ring of the bicyclic system, while the carbonyl group is located in space in such a way that it influences the resonance absorption of the $H_{(4)}$ proton due to a non-bonding interaction. The signal of the $H_{(4)}$ proton is displaced downfield, the strongest signal (~ 1 p.p.m.) being observed for the formyl derivative[126].



(XLII)

It has been shown by ^1H NMR[184] that even at very low temperatures the free rotation of the dimethylamino-group of the isoindole (XLII, R = H) is unhindered.

5. Photoelectron Spectra

A correct method for estimating the energy of the highest occupied molecular orbital (HOMO) may be based on the first ionisation potential (IP) of the molecule. Information about the ionisation potential can be obtained from photo-electron spectra. The photoelectron spectra of isoindole and other *o*-quinonoid heterocycles were determined in 1976 by three groups of investigators[15,116,127]. In all cases a helium lamp served as the source of radiation. Inspection of the experimental and calculated Franck–Condon (vertical) values of IP[114,124] shows that not all methods of calculation yield satisfactory results.

The method of structural representations for the theoretical description of electronic spectra, the foundations of which were laid by Simpson[130], has been used successfully to predict the IP in studies by Koenig and coworkers[127,131,185]. The method has been used[127] to calculate the IP of 2-methylisoindole.

Inspection of the data in Table 3 permits the following conclusions.

(1) the IP diminishes successively in the series pyrrole–indole–isoindole, i.e. an increase in the size of the aromatic system entails an increase of the HOMO energy.

(2) The nitrogen-containing heterocycles (I), (II), and (LVII) have more marked π-donor properties than their oxygen and sulphur analogues.

(3) the benzo[*c*]-derivatives of the monocyclic compounds (LVII) have lower IP (higher HOMO) than the benzo[*b*]-derivatives, i.e. the heterocycles with the *o*-quinonoid structure have a more pronounced π-donor capacity than their positional isomers.

Table 3. The first ionisation potentials (IP, eV) of *o*-quinonoid heterocycles, their positional isomers, and the monocyclic compounds.

X			
>N—CH$_3$	7.95 [127]	7.87 [127]	7.2 [116]
—S—	8.86 [129]	8.47 [121]	7.7 [116]
—O—	8.89 [129]	8.29 [121]	8.0 [116]

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

The capacity of isoindoles for the formation of charge-transfer complexes (CTC) on interaction with electron acceptors may be regarded as confirmation of the existence of the π-donor capacity. A stable complex of 2-methylisoindole with trinitrobenzene has been described[14]. Similar complexes had been obtained earlier for pyrrole, indole, and other heteroaromatic compounds.

6. Electronic Spectra

The above photoelectron spectroscopic data show that the *o*-quinonoid heterocycles require less excitation energy than their structural isomers. This conclusion is also confirmed by a comparison of the electronic spectra of indoles and isoindoles. Whereas the long-wavelength absorption maximum in the spectra of indoles is displaced towards shorter wavelengths compared with that in the naphthalene spectrum, in the spectra of isoindoles it is actually at longer wavelengths. Analysis of the ultraviolet spectra of isoindoles permits certain generalisations. Three regions of absorption in the ultraviolet are characteristic of 2*H*- and 2-alkyl-isoindoles:

(a) Band *A* (230 ± 5 nm) with an intensity lg ε = 4.2–4.5 (one maximum);

(2) band *B* (260–290 nm) with an intensity lg ε = 3.1–3.3 (from one to three maxima);

(3) band *C* (320–350 nm) with an intensity lg ε = 3.6–3.7; solutions of isoindoles in n-hexane absorb in region *C* in the form of several closely spaced maxima, which is associated with the vibronic interactions.

A bathochromic shift of bands *A*, *B*, and *C* has been observed for 2-arylisoindoles compared with 2-alkyl-substituted derivatives. The intensity of the bands in regions *A* and *C* does not then change, while the intensity of the *B* band increases somewhat. The introduction of phenyl substituents in the 1,3-positions of isoindole results in a bathochromic shift of the absorption in region *C* accompanied by a slight hyperchromic effect for bands *B* and *C* compared with the parent isoindole and 2-alkylisoindoles.

The absorption spectra of benzoisoindoles are determined by the type of annelation of the benzene ring. Thus benzo[*e*]- and dibenzo[*e*,*g*]-isoindoles[15] absorb in the same region of the ultraviolet spectrum as the parent isoindole, while the long-wavelength absorption maximum in the spectrum of benzo[*f*]isoindole is displaced to the visible region[15]. Furthermore, the intensity of the *B* band is much higher in the spectra of benzoisoindoles.

Calculations of the energies of the singlet–singlet transitions for isoindole and its benzo-derivatives have been made by semiempirical methods in the π-electron approximation[15, 113,115,118,134]. Calculated data closest to the experimental values have been obtained by Rettig and Wirz[15] and Klasinc et al.[115] The directions of polarisation of the absorbed light in the transitions to the S_1 and S_2 states of the isoindoles (XXXIV, R = Me) and (IX, R = Me) have been predicted on the basis of calculations[15] and then confirmed experimentally. Tests showed that the $S_0 \rightarrow S_2$ transitions in the above compounds are polarised along the major molecular axis, while the $S_0 \rightarrow S_1$ transition, which should have been polarised along the short molecular axis, in fact exhibits a mixed polarisation due to the excess vibrational energy, which the molecule receives on excitation[15].

A phenomenological approach to the analysis of the electronic spectra of isoindoles has been made[118] on the basis of the indene anion model as a general perturbed system. An intense fluorescence corresponds to the long-wavelength absorption band of isoindoles. It has been shown[15] that in 2-methylisoindole 8% of the excitation energy is emitted in the form of phosphorescence with a lifetime of 0.4 s, and that its first triplet level is lower relative to naphthalene, for which E_T = 21266 cm^{-1} according to Gordon and Ford[129].

The mechanism of the spectral chemiluminescence of two arylisoindoles has been investigated[135]. The authors concluded that a cooperative effect is responsible for the excitation of electrochemiluminescence.

7. Infrared Spectra of Isoindoles

No systematic studies have been made of the infrared spectra of derivatives of isoindoles in order to discover and assign their characteristic absorption bands. Within the framework of a study of the tautomerism and association of cyclic amidines, their infrared spectra, including those of 1-aminoisoindole, have been obtained[48]. Theoretically, three tautomeric structures are possible for 1-amino-isoindoles, but, according to the results of the study of its infrared spectra in the solid state and in solution, it exists mainly in the form (XVI, $R^1 = R^2 = H$, $R^3 = NH_2$).

8. Mass Spectra of Isoindoles

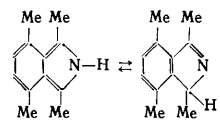
A general characteristic feature of all the known data for the mass-spectra of isoindoles may be noted, namely the fact that the most intense peak in the spectrum is that of the molecular ion M^+. In the majority of studies of isoindole the mass-spectrometric data are confined to those for M^+. The complete set of mass-spectrometric data is available for the following isoindoles: compound (III)[20,27], 2-methylisoindole[44], compound (IX)[15], compound (X)[15], 2-butylisoindole[20], and 2-ethyl-1,3,4,7-tetramethylisoindole[76]. The fragmentation of 1,3-diphenylisoindole and 1,3-diphenylisobenzofuran has been analysed in detail in only one study[136].

9. The Tautomerism of Isoindoles

One of the most characteristic features of isoindole (III) is its ability to undergo rapid tautomeric transformations into the corresponding 1*H*-isoindoles (isoindolenines) (IIIa). Since the *o*-quinonoid structure (III) and the isoindolenine structure (IIIa) differ insignificantly in their thermodynamic stabilities, which precludes the isolation of the tautomeric forms in a pure state, the equilibrium (III) ⇌ (IIIa) was investigated by ultraviolet and infrared spectroscopy and mainly by NMR.

The first studies[20,27,94] on the NMR spectra of isoindole (III) at low temperatures (−40 °C) showed that this compound is a mixture of tautomers (III) and (IIIa) with the *o*-quinonoid structure predominating in the equilibrium. However, it was found later[123] that, when a mixture of compounds (III) and (IIIa) is dissolved in solvents of different polarity, the content of compound (III) in solution increases with time, its accumulation obeying a kinetic first-order law ($T_{1/2}$ = 16 min). It has been established by ^{1}H NMR that the content of the *o*-quinonoid structure (III) increases at −40 °C in initial mixtures in solvents of different polarity. In all cases the NMR signals corresponding to the isoindolenine structure (IIIa) disappear altogether after a definite time interval, i.e., regardless of the polarity of the medium, the process stops only when the isoindolenine form (IIIa) is completely (or almost completely) converted into the thermodynamically more favourable *o*-quinonoid structure (III).

1-Methyl-, 1,3-dimethyl-, and 1,3,4,7-tetramethyl-isoindoles as well as the parent isoindole (III) exist in solution in equilibrium with their isoindolenine tautomers and the equilibrium position depends significantly on the nature of the solvent employed[98]. The study of deuterium exchange for 1-phenylisoindole confirmed unambiguously the earlier observation of equilibrium between isoindole and its isoindolenine tautomer[98,123]:



(XLIII) (XLIV)

It has been shown with the aid of infrared, ultraviolet, and ^{1}H NMR spectra that the isoindole (XLIII) exists in solution as well as in the solid state in a mixture with its tautomer (XLIV) with the latter predominating[28]. It has been found that the state of tautomeric equilibrium is greatly influenced by the ability of solvents to form intermolecular hydrogen bonds with compound (XLIII).

The position of the isoindole–isoindolenine equilibrium depends on two effects[137]—electronic and steric. Electron-donating groups in the 1- and 3-positions of the bicyclic system stabilise the isoindolenine tautomer. For example,

the amount of the isoindolenine tautomer in deuterochloroform is 9% for compound (XXI, R = Ph), 31% for (XXI, R = 4′MeOC$_6$H$_4$), and 100% for (XXI, R = OEt). On the other hand, electron-accepting groups increase the content of the *o*-quinonoid structure in the tautomeric mixture in deuterochloroform. 5-Methyl-1,3-diphenylisoindole[60], 1-cyanoisoindole[104], 1-methoxycarbonylisoindole[13], and 1,3-dimethoxycarbonylisoindole[11] have the 100% *o*-quinonoid structure. On the other hand, the steric effect is manifested in compounds (XLIII), where there are two peri-interactions involving the methyl groups in the 1,7- and 3,4-positions and exerting a destabilising influence. In the tautomeric form (XLIV) one of these interactions has been eliminated which is undoubtedly associated with a considerable energy gain[137].

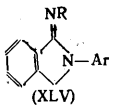
The type of annelation of benzene rings to the isoindole molecule influences significantly the position of the tautomeric equilibrium. In agreement with quantum-chemical calculations[1], the isoindoles (X, R = H)[22] and (XIII, R = H)[23] exist exclusively in the *o*-quinonoid form, while benzo[*f*]-isoindole (IX, R = H) exists preferentially in the corresponding tautomeric isoindolenine form (IXa), but the formation of an adduct with *N*-phenylmaleimide confirms the presence of a certain amount of the tautomer having the isoindole structure (IX)[176]. Halogen (fluorine[94,95,97], chlorine[25], and bromine[24]) atoms in the isoindole ring suppress the formation of the isoindolenine tautomer and stabilise the system as a whole compared with the parent compound. The presence of the isoindolenine tautomer has not been observed for any of the halogenoisoindoles. We mentioned above the unsuccessful attempt to isolate both tautomeric forms of isoindoles. However, in the case of compound (XXVI, R = H) each tautomeric form was obtained in a pure state. When a solution of the methylamide (XXVIII, R = H) in DMF is treated with sodium carbonate, the isoindolenine (XVI, R^1 = CONHMe, R^2 = H, R^3 = Ph) is formed. On treatment with acid, this compound is converted into the tautomer with the isoindole structure[77].

IV. CHEMICAL PROPERTIES

1. Alkylation of Isoindoles

The alkylation of isoindoles unsubstituted at the nitrogen atom can proceed in two ways: either at the N$_{(2)}$ atom with formation of 2-R-isoindoles or at the C$_{(7)}$ (or C$_{(3)}$) atom of the pyrrole component of the bicyclic system. Thus methylation of 1,3-dimethoxycarbonylisoindole with diazomethane in ether gives a high yield of the *N*-methyl derivative[21]. Alkylation of aminoisoindole with phenacyl bromide also involves the N$_{(2)}$ ring nitrogen atom with formation of the salt (XVIII, R^3 = NH$_2$, R^4 = CH$_2$COPh)[138].

Interesting results have been obtained[49,139] in the alkylation of cyclic amidines having the general formula (XLV, R = H) with dimethyl sulphate (DMS). The interaction of compound (XLV) with DMS gives rise to the corresponding *N*-methylisoindolenine methosulphates (XLV, R = Me). The bases (XLV, R = Me) react with DMS to form salts, which are converted into the isoindoles (XLII, R = H) on treatment with bases[139]. 1,3- and 1,4-Bis(1-dimethylamino-2-isoindolyl)benzenes have been obtained similarly from the corresponding cyclic amidines[55]



(XLV)

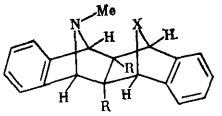
The alkylation of 1-alkoxyisoindolenines[43,56] with trialkyloxonium fluoroborates involves the nitrogen atom N$_{(2)}$ with formation of the salts (XVIII, R^3 = OAlk), from which the isoindoles (XVII, R^1 = OAlk) can be obtained by treatment with bases. The vast majority of instances of the alkylation of isoindoles unsubstituted at the N$_{(2)}$ atom involve the preliminary generation of isoindole anions with the aid of alkali metal hydrides[28,65,66,94,140,141], alkoxides[77,78], or hydroxides[58] in suitable solvents. Thus the alkylation of the esters (XXVIIIb, R = H) and the amides (XXVIIIa, R = H) at the ring nitrogen atom has been described in patents[65,66].

The alkylation of the 3-(4′-chlorophenyl)-1-ethoxyisoindole anion with alkyl halides[42,141] or bromoacetic esters[140,180–182] involves the C$_{(3)}$ carbon atom with formation of racemic isoindolenines of the type (XVI, R^3 = OEt). On alkylation with benzyl bromide, the anion of the isoindole (XLIII) yields 1-benzyl-1,3,4,7-tetramethyl-1*H*-isoindolenine[28]. The anions of the methylamides (XXVIIIa, R = H) are alkylated with ethylene bromohydrin[78] and methyl iodide[77] at the N$_{(2)}$ ring nitrogen atom, but in the latter case the *C*-alkylation product is also isolated. More complex compounds containing the ring of the isoindole (IV) are alkylated by dialkyl sulphates at the N$_{(1)}$ atom in the presence of bases[58].

2. The Diels–Alder Reactions

(a) The Addition of Dimethyl Acetylenedicarboxylate (DMAC)

Isoindoles combine extremely readily with DMAC to form products with different proportions of isoindole and DMAC[2]. Thus Wittig showed[1] that 2-methylisoindole forms a 2:1 adduct (XLVI) with DMAC. However, the majority of isoindoles give rise to 1:1 adducts (XXXII, R^1 = COOMe), i.e. substituted 7-azabenzonorbornadienes[92,187].



(XLVI)

The reactions of isoindoles with DMAC are exothermic. An increase of the temperature of the reaction mixture in the presence of an excess of DMAC can entail the deamination of 7-azabenzonorbornadiene and the formation of the corresponding naphthalene, which has been observed[108,142]. On reaction with DMAC, certain 2*H*-isoindoles form 1:2 adducts with the structure (XXXII, R = MeOOCC = CHCOOMe, R^1 = COOMe). This applies particularly to tetrachloro-(bromo)isoindoles. The isoindole (XLIII) reacts with DMAC at room temperature to form a 1:1 adduct of the type (XXXII), which rearranges to a 1:2 adduct of the type (XLVII) on refluxing with DMAC in benzene. *N*-Ethyl- and *N*-n-butylisoindoles react with DMAC at 0 °C to give the corresponding compounds (XLVII), the mechanism of the formation of which has been described[137]. Ethyl propiolate does not form adducts with isoindoles[19].

(b) The Addition of Dehydrobenzenes to Isoindoles

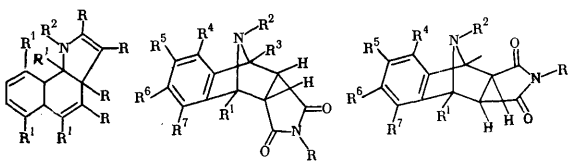
Isoindoles readily combine with dehydrobenzene to form derivatives of 7-azadibenzonorbornadienes. Wittig showed for the first time[1] that *N*-methyl- and *N*-phenyl-isoindoles react with dehydrobenzene to form the adducts [XXXII, R^1 + R^1 = (CH = CH)$_2$], which can react further with an

excess of dehydrobenzene to form anthracene derivatives[1]. Dehydrobenzene, generated in different ways, reacts with 2-methyl-1,3-diphenylisoindole to form adducts of the above type[143]. The reaction of 2,4,7-trimethyl-1,3-diphenylisoindole with dehydrobenzene gives rise to the corresponding derivatives of 7-azadibenzonorbornadiene[144].

A new method of generating dehydrobenzene from chlorobenzene and the lithio-derivatives of tetramethylpiperidine has been tested in relation to the synthesis of 7-methylazadibenzonorbornadiene from 2-methylisoindole[145]. A large group (more than 40 compounds) of substituted 7-azadibenzonorbornadienes have been obtained from substituted isoindoles and dehydrobenzenes (15 types), dehydronaphthalenes, and heteroarynes (8 types)[14]. A series of new adducts of isoindoles with dehydrobenzene and dehydronaphthalene have been used in the oxidative deamination reaction in order to obtain new derivatives of anthracene and benzanthracene which are otherwise difficult to synthesise[146]. Krick and Vernon[144] explained the extremely unusual result of the reaction of 2-benzyl-1,3,4,7-tetramethylisoindole with dehydrobenzene by the deamination of the 7-azadibenzonorbornadiene derivative, the formation of the corresponding anthracene, and the subsequent cycloaddition of dehydrobenzene in the 9,10-positions of the latter.

(c) The Addition of Maleic Acid Derivatives to Isoindoles

The formation of an adduct with *N*-phenylmaleimide is the usual method of identifying isoindole[93,103]. The addition of *N*-phenylmaleimide to isoindoles can theoretically lead to two products: the *endo*-product (XLVIII) and the *exo*-product (XLIX). One of the most correct methods of determining the configuration of the adducts is ^{1}H NMR, since the patterns of the signals due to the protons in the 1-, 4-, 5-, and 6-positions in these compounds are significantly different[20,96]. A mixture of compounds (XLVIII) and (XLIX), with the *exo*-adduct predominating, is obtained from isoindole and *N*-phenylmaleimide. If this mixture is heated in xylene, then the *endo*-adduct is transformed into the thermodynamically more stable *exo*-isomer[20,27].



(XLVII) (R=COOMe) (XLVIII) (XLIX)

Benzo[*e*]isoindole, benzo[*f*]isoindole, and dibenzo[*e*,*g*]isoindole also form an adduct with *N*-phenylmaleimide[22,23,96], although, according to spectroscopic data, benzo[*f*]isoindole has the isoindolenine structure[95]. The geometry of the adduct of isoindole (X, R = H) with *N*-phenylmaleimide precludes its assignment to a definite type, since it dissociates in concentrated solutions and the ^{1}H NMR spectrum reflects a mixture of the initial substances[22].

4,5,6,7-Tetrafluoro-[94] and 4,5,6,7-tetrachloro-isoindoles[25] react with *N*-phenylmaleimide to form the corresponding exo-adducts, while the π-electron system of tetrabromoisoindole is so deactivated that it does not form an adduct with maleic anhydride[24]. It has been shown[97] that treatment of tetrafluoroisoindole with *N*-phenylmaleimide gives rise to a mixture of the *exo*- and *endo*-adducts, which can be separated by column chromatography on silica gel. This is perhaps the only example where the *exo*- and *endo*-adducts were isolated in a pure state.

The isoindole (XLIII) and maleic anhydride form an adduct, which has the structure (XLVIII) or (XLIX) in the solid state; however, in solutions the adducts associate into the initial substances, which react anew but now with formation of adducts of the Michael type[137]. The cyclic 1:1 adduct of the isoindole (XI, X = Cl) with 4-phenyl-1,2,4-triazoline-3,5-dione has been described[25]. 2R-Isoindoles form adducts with dienophiles just as readily as the 2*H*-derivatives.

N-Methylmaleimide reacts with 2-ethoxycarbonylisoindole and 2-methyl-4,5,6,7-tetrafluoroisoindole to give a mixture of *exo*- and *endo*-adducts according to ^{1}H NMR data[96]. Mixtures of the same composition are also formed by the reaction of *N*-phenylmaleimide with the isoindole (XI, R = Me, X = F)[88]. Adducts of the isoindoles (XI, X = Br, R = Me) with *N*-phenylmaleimide could not be obtained[16]. 2-Acetylisoindole *in statu nascendi* reacts with *N*-phenylmaleimide to produce a low yield of the *exo*-adduct[20]. The isoindole (XI, X = F, R = CH_2Ph) reacts with *N*-phenylmaleimide at 0 °C to form the adduct (XLVIII). A series of endo-adducts have been obtained from the isoindole (XL) by the reaction with *N*-methyl- and *N*-phenyl-maleimides and also with 1,4-benzoquinone[108].

The isoindole (XLII) reacts readily with maleimide and *N*-phenylmaleimide to give high yields of adducts, which we assign to the *endo*-series on the basis of the ^{1}H NMR spectra quoted in the relevant communication[147]. 1-Alkoxy-2-methyl-isoindoles react with maleimide derivatives to form 1:2 *exo*-adducts; initially electrophilic addition probably takes place at the free $C_{(3)}$ position in the isoindole and then the usual addition at the $C_{(1)}$ and $C_{(3)}$ carbon atoms[43]. The addition of 1,4-epoxy-1,4-dihydronaphthalene to 2-methylisoindole gives rise to the isomeric *exo-exo*-adduct (XLVI, X = O) and *exo-endo*-adduct, which were separated chromatographically[9].

3. Isoindoles under the Conditions of Attack by an Electrophile

(a) Electrophilic Addition Involving Isoindoles

The protonation of isoindoles—the simplest example of the electrophilic addition reaction—takes place at the $C_{(1)}$ or $C_{(3)}$ carbon atom in view of their symmetrical structure. The ionisation constants of the two isoindoles (XXII, R = R^5 = Me) and (XXII, R = Ph, R^4 = Me) have been determined spectrophotometrically[148]. The greater basicity of isoindole derivatives compared with that of the corresponding *N*-methyl- and *N*-phenyl-indoles can be accounted for by the greater resonance stabilisation of the latter. There are virtually no data on the protonation of the asymmetrically substituted isoindole (VIII). On protonation, the isoindoles (XLII, R = H)[139] and (XVII, R^1 = OAlk) form cations with the structures (XVIII, R^3 = NMe_2 or OAlk) respectively. This has been confirmed by ^{1}H NMR.

Comparison of the ultraviolet spectroscopic data for tetra- and penta-substituted isoindoles (XXII) in neutral and acid media revealed interesting features[60]. It was found that the methyl group in the 4-position in isoindole promotes the formation of the cation. The transition of the $C_{(1)}$ or $C_{(3)}$ atom from trigonal to tetrahedral hybridisation enables one of the phenyl substituents to deviate from the plane in which the methyl group at the $C_{(4)}$ or $C_{(7)}$ atom is located, which entails a decrease of steric strain, favouring an increase of the fraction of the isoindolenine form of the cation[60].

Examples of reactions involving electrophilic addition to isoindoles have been published[25,55,70,77,139]. It was found that, as a result of electrophilic addition, the reaction of

DMAC with isoindoles of the type (XVII, R^1 = SAlk) gives rise to the product (VIII, R^1 = SAlk, R^3 = MeOOCC = CHCOOMe)[70]. An analogous type of addition has been observed[25] in the reaction of azodicarboxylate esters with tetrachloroisoindole. The isoindoles (XLII, R = H) readily add to phenyl isocyanates and isothiocyanates, giving rise to high yields of the corresponding 3-substituted derivatives[55,139]. The reaction of 2-methyl-1-phenylisoindoles with methyl isocyanate leads to the methylamide of 2-methyl-3-phenylisoindole-1-carboxylic acid[77].

(b) Electrophilic Substitution Reactions of Isoindoles

The rates of the simplest electrophilic substitution reaction (deuterium exchange) in the series of bicyclic 10-π-electron compounds have been determined[149] and it was found that 2-methylisoindole is more reactive by four orders of magnitude than 1-methylindole.

The available information about the electrophilic substitution reactions of isoindoles is scanty. Thus the treatment of the isoindoles (XLII) with acetic anhydride or benzoyl chloride leads to acyl derivatives as a result of the electrophilic substitution reaction[139]. Interesting compounds have been obtained via the electrophilic substitution mechanism from 1,2-disubstituted isoindoles and the trimethylsilyl ester of 6-isocyanatopenicillanic acid[150]. 2-Benzyl-1-methoxycarbonylisoindole does not undergo the electrophilic substitution reactions (the Mannich reaction and acetylation)[13].

4. Isoindoles under the Conditions of Attack by a Nucleophile

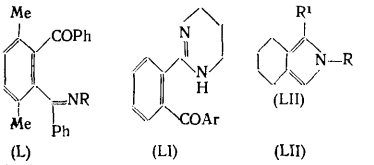
Nucleophilic substitution of isoindoles has been mainly studied for 1-alkoxyisoindoles having the structure of isoindolenines and structurally similar to the iminoesters of carboxylic acids. All the reactions described below can be readily understood and accounted for from this point of view. Thus the reaction of 1-ethoxyisoindole with primary aromatic and heterocyclic amines involves the substitution of the ethoxy-group by an arylamino-group[151]. More than 40 compounds have been obtained in this way. Benzylamine[152] and its substituted derivatives[151-152] as well as 2-(β-dialkylamino)-ethylamine[152] react with salts of 1-ethoxyisoindole to form the same products as in the reactions with the bases, but the yields are higher[56]. The reaction of 1-ethoxyisoindole with hydrazine produces 1-hydrazinoisoindole[56,152], while 3-aryl-1-ethoxyisoindole gives a high yield of aminophthalazines[42]. Phenylhydrazine and hydroxylamine are also capable of substituting an alkoxy-group in the 1,3-positions of the bicyclic system[56]. On being refluxed with aziridinium tetrafluoroborate in toluene, 1-ethoxyisoindoles give rise to the derivatives of imidazo[2,1-*a*]isoindole as a result of the nucleophilic substitution of the ethoxy-group and simultaneous cyclisation[40,41].

5. Heterocyclisation Based on Isoindole Derivatives

1-Amino-2-phenylisoindole and its hydrobromide are converted into 2-phenyl-5*H*-imidazo[2,1-*a*]isoindole on heating[138]. On heating in acetone, 2-aminoethylisoindoles cyclise to pyrazinoisoindoles[82,85]. On condensation with α-acetyl-γ-butyrolactone in acid, 1-aminoisoindole gives rise to a mixture of isomeric condensed pyrimidoisoindoles[153]. When a solution of 3-phenylisoindole-1-carboxamide in acetic anhydride was stirred with boron trifluoride etherate, an orange product, consisting of a derivative of imidazo[5,1-*a*]isoindole was isolated[77]. On prolonged refluxing with orthoesters in isopropyl alcohol, 1-hydrazinoisoindole forms triazoloisoindoles in moderate yields[154]. Tetrazoloisoindole is formed from 1-hydrazinoisoindole and nitrous acid in a high yield at a low temperature[155].

6. Oxidation of Isoindoles

Isoindoles are extremely sensitive to the action of atmospheric oxygen. Isoindoles unsubstituted at the $N_{(2)}$ atom can give rise to two types of products on mild oxidation: compounds containing two residues of the corresponding phthalimidine, which is observed in the oxidation of 1-methoxycarbonylisoindole[13], and tertiary alcohols of the type (XVI, R^1 = OH), with formation of a hydroperoxide of the type (XVI, R^1 = OOH) as an intermediate in the latter case[156]. The oxidation of isoindoles gives rise to a wide variety of products whose structure depends on the reagents employed and the reaction conditions. The reactions of permanganate in an alkaline medium with 1-cyanoisoindole[105] and 1,3,4,7-tetramethylisoindole[28] or of hydrogen peroxide in acetic acid[157] (or in alcohol[77]) with the isoindoles (IV, X = HC) and (XXVI, R = H) give rise to phthalic acid derivatives. Treatment of the isoindole (IV, X = HC) with chromium trioxide in an acid medium leads to *o*-benzoylbenzoic acid[157], while nitrous acid converts compound (XXII, R^4 = R^7 = Me) into 1,2-dibenzoyl-3,6-dimethylbenzene[156].



(L) (LI) (LII)

The self-oxidation of 1,2,3,4,7-pentamethylisoindole produces the corresponding phthalimide[76]. Benzophenones (L) are obtained by the self-oxidation of the isoindoles (XXII, R^4 = R^7 = Me, R^5 = R^6 = H). On the other hand, in the case of the isoindole (XXII, R = Ph) self-oxidation is achieved following additional irradiation with ultraviolet light and the imine (L) formed initially is converted subsequently under the experimental conditions into a phenanthridine derivative[156]. In the absence of oxygen the above isoindoles are entirely stable on both heating and irradiation. Oxidation of the isoindoles (XVII, R^1 = COOMe) with oxygen gives rise to the corresponding phthalimidines (XV)[13]. Irradiation of a solution of isoindole (XXVIIIa, R = Me) with access of air leads to a mixture consisting of the phthalimidine (XV, R^1 = Ph) and its 3-hydroxy-derivative[77]. Prolonged oxidation of solutions of 2-(γ-aminopropyl)isoindoles with oxygen and sometimes with $K_2Cr_2O_7$, $KClO_3$, and H_2O_2 leads to pyrimidoisoindoles and not to benzophenones (LI), as believed previously[166]. More than 40 compounds of this series have been described in a number of patents[158,165].

7. Reduction of Isoindoles

The catalytic hydrogenation of isoindoles in the presence of 10% Pd/C in ethanol[13] or in acetic acid[84] at a pressure of 3–5 atm gives rise to products of the addition of hydrogen to the pyrrole component of the molecule. Thus 1-methoxycarbonyl-2-phenylisoindole[13] and 2-γ-aminopropyl-1-arylisoindoles[84] form racemic mixtures of isoindolines under these conditions. Under the same conditions, the isoindole (VIII,

$R^1 = R^3 = COOMe$, $R^2 = Ph$) forms three products: the meso- and *d,l*-forms of the corresponding isoindolines[13]. The catalytic hydrogenation of the isoindoles (XXVIII, R^2 = 5-H or 5-Cl) in the presence of palladium chloride produces the same isoindoline[77]. Hydrogen adds readily only to the double bond of 2-vinylisoindoles on catalytic hydrogenation[79]. The use of Raney nickel as the catalyst of the hydrogenation of 2-(γ-methylaminopropyl)isoindole yields results similar to those of the catalytic hydrogenation on Pd/C, i.e. hydrogen adds to the pyrrole component of the molecule[86].

The final result of the hydrogenation reaction probably depends to a large extent on the nature of the substituents in the pyrrole component of the bicyclic system. Thus the hydrogenation of the isoindoles (XVII, $R^1 = COOMe$) yields products of the addition to the carbocyclic moiety with formation of compounds (LII), in contrast to 1-methoxycarbonyl-2-phenylisoindole mentioned above. A similar result has been obtained[167] in the hydrogenation (in the presence of the $Pd/BaSO_4$ catalyst) of the isoindole (VIII, $R^1 = CHO$, $R^2 = CH_2CH_2Ph$, $R^3 = Cl$)—the pyrrole (LII, $R^1 = CH_2OH$, $R = CH_2CH_2Ph$) was isolated as the hydrogenation product.

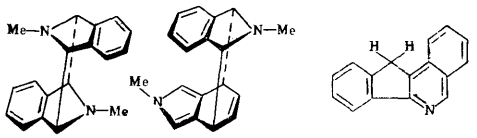
In all the known instances of the reduction of isoindoles with zinc dust in acetic acid, the corresponding isoindolines were obtained. This reduction method has been used for 4,5,6,7-tetrafluoroisoindole[94,95], benzo[*e*]isoindole[23], dibenzo-[*e,g*]isoindole[22], and 1,2-dimethyl-3-phenylisoindole[32]. It is of interest to note that in the latter case the mixture of diastereoisomers formed as a result of the reaction was resolved. Similarly the reduction of the isoindole (XLIII) with zinc dust in acetic acid yielded the isomeric *trans*- and *cis*-iso-indolines, which were separated. The catalytic hydrogenation of compound (XLIII) in the presence of PtO_2 in alcohol gives rise to mixtures of isoindolines with similar compositions[28].

8. Other Reactions of Isoindoles

Isoindoles are known to undergo reactions involving a functional group but not the ring. Thus the nitrile of isoindole-1-carboxylic acid is smoothly converted into the amide on treatment with 10% alkali[104]. The phthalyl protecting group is removed almost quantitatively from the isoindole (VIII, $R^1 = R^3 = Ph$, $R^2 = NCOC_6H_4CO$) on treatment with hydrazine[110]. The isoindole (XXVI, $R = CH_2CH_2OH$) is acetylated under different conditions, with the preferential formation of diacetyl derivatives—the products of the reaction involving the oxygen atom of the alcoholic group and the nitrogen atom of the *N*-methylcarbamoyl group[78,79]. On hydrogenation in methanol with added sodium methoxide and in the presence of the $Pd/BaSO_4$ catalyst, the isoindoles (VIII, $R^1 = CHO$, $R^3 = Cl$) retain the isoindole structure but lose chlorine atoms, forming 1-formyl-2R-isoindoles in 80% yield[167]. The isoindole (XXVIIIa, $R^2 = Cl$) is dehydrochlorinated similarly[77]. On being refluxed with an excess of hydrazine in ethanol for 2 h, the 5,6-dibenzoyl-1,2,3-trimethylisoindole gives rise to derivatives of 6,7-diazabenzo-[*f*]isoindole[75].

A number of coloured products (IV, X = RC) are formed on condensation of 1-phenylisoindole with aldehydes in pyridine with very low yields[62,169]. When the isoindole (XLIII) is heated with metal (copper, nickel, manganese, etc.) acetates, the corresponding coloured octamethyltetrabenzoporphyrins are formed. Similar molybdenum and cobalt compounds have been isolated in the form of complexes in which the central metal atom coordinates additionally other ligands (for example, pyridine, etc.)[137,169].

Under the conditions of the Vilsmeier reaction, the isoindole (XXVIIIa) forms 5-chloro-1-dimethylaminomethylene-3-phenyl-1*H*-isoindole, i.e. the carbamoyl group is eliminated and the $C_{(1)}$ atom is formylated[77].



(LIII) (LIV) (LV)

The photolysis of a solution of the isoindole (XXXIV, R = Me) leads to a 60% yield of the $[{}_{\pi}4_S + {}_{\pi}4_S]$ photodimer (LIII). Together with compound (LIII), the isomeric dimer (LIV) was isolated in 7% yield. When both dimers are irradiated with ultraviolet light at 254 nm, they dissociate and the initial isoindole is formed. Pyrolysis converts the isoindole (XXXIV, R = Me) into a condensed isoquinoline (LV)[170].

9. Practically Useful Properties of Isoindoles

In patents there are indications of the possibility of practical applications of isoindole derivatives, particularly in medicine. Thus antihypertonic[152], anti-inflammatory[152], contraceptive[138], and anorectic[65,66] effects and the sedative[87] and stimulating[81,84] influences on the central nervous system by various isoindole derivatives have been reported.

A series of preparations have been tested in electroluminescent systems[67] and as agricultural fungicides[85].

V. AROMATICITY OF *o*-QUINONOID HETEROCYCLES

The data on the physical and chemical properties of isoindole discussed above indicate a number of characteristic features of this system and other *o*-quinonoid heterocycles of type (II). In the discussion of the differences between the properties of indole and isoindole, attention must be concentrated on the differences between the degrees of their aromaticity.

A common characteristic of indole and isoindole is the presence of the 10-π-electron cloud and the identity of the electronic configurations of the atoms. The only difference, which determines the entire set of the physicochemical properties of systems (I) and (II), is that between the positions of the heteroatom in the 10-π-electron cloud and the consequent difference between the perturbations in the two cases.

Isoindole derivatives are more reactive than the corresponding indoles; isoindole itself is an extremely unstable readily polymerisable compound, i.e. its chemical behaviour does not indicate its aromaticity. Nevertheless, according to data obtained by various quantum-chemical computational methods[114,132,133,172,173], isoindole possesses a significant resonance energy, although it is smaller than that of indole (Table 4).

The resonance stabilisation of isoindole is indirectly confirmed by the spontaneous and irreversible transformation of the isoindolenine form into the isoindole form[123].

Consequently it is necessary to explain two mutually exclusive facts, namely why is isoindole so reactive if it is at the same time aromatic in the usual sense of the term.

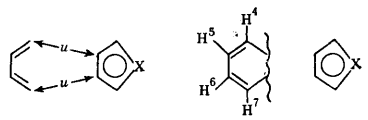
We may point to several studies[15,116,123,124,175] whose authors noted the above contradiction and attempted to resolve it. Apparently the best founded hypothesis,

capable of reconciling the high reactivity of *o*-quinonoid heterocycles with their aromaticity, is that put forward by Bornstein and coworkers[124], according to which the *o*-quinonoid heterocycles (II) consist of adjacent but in essence non-interacting π-electron systems and therefore possess a wide region of aromaticity due to the presence of the five-membered heterocyclic rings together with the reactivity imparted to the bicyclic system (II) by the adjacent butadiene component.

Table 4. The resonance energies of indole (I, X = NH) and *o*-quinonoid heterocycles (II).

Heterocycle	In units of β (Ref.172)	In units of β (Ref.173)	in kcal mol^{-1} (Ref.114)
(II) (X = NH)	0.29	0.32	11.6
(II) (X = S)	0.25	0.29	9.3
(II) (X = O)	0.02	0.11	2.4
(I) (X = NH)	0.47	0.38	23.8
(XLIV) (X=NH)	—	—	8.4

As a structural equivalent of the above hypothesis, it has been suggested[124] that *o*-quinonoid heterocycles be represented with the aid of formulae of type (LVI). The above structural ideas were first used[127] to calculate the ionisation potential of 2-methylisoindole. They have been confirmed primarily by the spin–spin interaction constants for isoindole and other *o*-quinonoid heterocycles[15,115,123–125]. According to Crews et al.,[125] the spin–spin interaction constants of the $H_{(4)}$–$H_{(7)}$ vinyl protons, obtained for various *o*-quinonoid systems (LVII), or more precisely the ratio $J_{rel} = J_{H_{(5)}-H_{(6)}}/J_{H_{(4)}-H_{(5)}}$, can serve as a characteristic of the degree of delocalisation of electrons in the butadiene fragments indicated.



(LVI) (LVII) (LVII)

Analysis of the data in Table 5 shows that, if the degree of delocalisation of electrons can indeed be estimated with the aid of J_{rel}, the implication is that the electron distribution in the carbocyclic component of *o*-quinonoid heterocycles is insensitive to perturbations in the five-membered rings. Consequently the constancy of J_{rel} for systems with such a widely variable stability (from the extremely unstable isobenzofuran to the comparatively stable isothionaphthene) can be understood only on the basis of the structural representations (LVI).

The subsequent discussion will be based on the resonance energies of structures (I), (II), and (LVII) calculated by Dewar. According to Dewar[128], the resonance energy of butadiene is zero. Consequently the difference between the calculated Dewar resonance energies of isoindole and pyrrole makes it possible to estimate the degree of stabilisation (annelation energy) as a result of the interaction in compound (LVII) between the butadiene and the five-membered heterocycle along side c. The annelation energy of butadiene and the five-membered heterocycle corresponding to the interaction along side *b* can be determined similarly.

Analysis of experimental data shows that, in contrast to heterocycles with the Kekulé structure, in which the annelation energy is ~15.4–18.8 kcal mol^{-1} (*o*-quinonoid heterocycles have an extremely insignificant annelation energy of 0.8–3 kcal mol^{-1}), annelation along side c of the second ring in compound (LVII) leads to only a very slight stabilisation of the system as a whole.

The structural representations (LVI) can be confirmed by comparing the bond orders of indole and isoindole. In the carbocyclic part of isoindole they are in essence the same as in acyclic polyenes, whereas the bond orders in the five-membered ring are close to those found for the monocyclic compounds (LVII).

Table 5. The spin–spin interaction constants (SSIC) for a series of derivatives of *o*-quinonoid heterocycles.

SSIC, Hz	(II) (X = NH) [123–124]	(XXXIV) (R = Me) [15]	(VIII) (R^1=R^2=Ph, R^3 = Me) [125]	(II) (X = O) [116]	(II) (X = S) [116]	(II) (X = Se) [124]
$J_{H(5)-H(6)}$	6.29	6.28	6.39	6.22	6.35	6.79
$J_{H(4)-H(5)}$	8.49	8.60	8.63	8.52	8.64	9.16
J_{rel}	0.74	0.73	0.74	0.70	0.72	0.74

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

If the above considerations are valid, then one must explain from the above standpoints the entire set of properties of *o*-quinonoid heterocycles, particularly isoindole. This can be done within the framework of the method of perturbed molecular orbitals (the PMO method)[128], in which *o*-quinonoid heterocycles are treated as combined residues of butadiene and the monocyclic π-system along side c in (LVI).

The diagram for the interaction of the molecular orbitals of butadiene and pyrrole, leading to the formation of the π-electron system of isoindole, obtained as a result of such treatment, is illustrated in the Figure taking into account the first- and second-order perturbations.

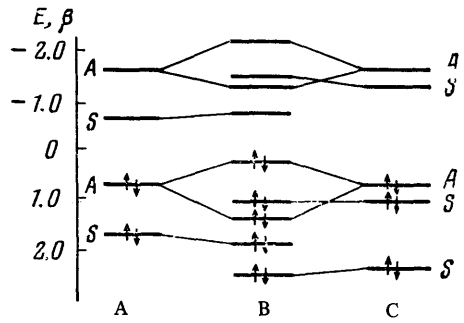


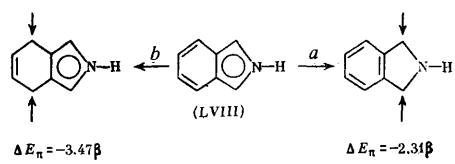
Diagram illustrating the interaction of the orbitals in the formation of the π-electron system of isoindole (B) by combining butadiene (A) and pyrrole (C).

When the residues of butadiene and of the monocyclic π-electron system of pyrrole are combined, two types of interaction are observed.

(1) Interaction between the highest occupied molecular orbitals (HOMO) of butadiene and pyrrole with the same energies, which leads to a decrease of the difference between the energies of the HOMO and the lowest unoccupied molecular orbitals (LUMO), i.e. is responsible for the low value of the first-ionisation potential and the long-wavelength absorption maximum; this type of interaction does not entail an energy gain (i.e. the stabilisation of the compound). Since the HOMO is antisymmetric in the symmetry plane $\sigma_v(y)$ and the energy of the interaction under consideration is independent of the nature of the heteroatom, all the *o*-quinonoid heterocycles exhibit a similar reactivity.

(2) Interaction with unfilled molecular orbitals, which leads to a slight decrease of the lowest occupied (symmetrical) molecular orbital of both butadiene and the monocyclic compound; this interaction depends on the nature of the heteroatom and is responsible for the annelation energy. In other words, the nature of the "aromaticity" of *o*-quinonoid heterocycles (II, X = NH, O, or S) is the same as that of the corresponding monocyclic compounds.

The structural ideas examined above should also account for the exclusively high reactivity of the *o*-quinonoid heterocycles (II) and in the first place for their tendency to enter into the Diels–Alder reaction. According to the structural representation (LVIII), there is a possibility of two types of cycloaddition reactions: to the pyrrole ring and to the carbocyclic part of the molecule. The energy of activation of π electrons (ΔE_π) in the molecule or, in other words, the reactivity of the molecule is determined mainly by the difference between the energy of the π electrons in the transition state and the energy of the π electrons of the reactants[128]. The formation of transition states in the above instances is illustrated graphically below (the arrows indicate the direction of cycloaddition) together with the calculated energies of activation of π electrons; the complete absence of interaction between the butadiene and pyrrole π-systems is postulated:



(LVIII)

$\Delta E_\pi = -3.47\beta$ $\Delta E_\pi = -2.31\beta$

Both values of ΔE_π presented are significantly smaller than for pyrrole itself and indicate an appreciable increase of the reactivity of isoindole.

Special mention should be made of the fact that the calculated activation energy for pathway *a* is smaller than that necessary for attack on the isolated butadiene fragment (pathway *b*). The activation energy in Diels–Alder reactions in relation to *o*-quinonoid heterocycles can be regarded as comprising two contributions: (1) the endothermic contribution due to the decomposition of the π-electron system of the five-membered ring and (2) the exothermic contribution due to the formation of the benzene ring on cycloaddition. The ratio of these two contributions is determined by the height of the activation barrier and, when account is taken of the considerations adduced above, it is clear that the higher resonance stabilisation of the "parent" five-membered heterocycle entails a corresponding decrease of the reactivity of the *o*-quinonoid heterocycle. Thus isobenzofuran, derived from the "weakly aromatic" furan, is much more reactive than isothionaphthene or isoindole, which are derived from more aromatic monocyclic compounds.

During the preparation of the manuscript for printing, a number of studies on the chemistry of isoindole were published. Thus-2-t-butylisoindole[208,213], 2-methylbenzo[*f*]isoindole[192,195], 4,7- and 5,6-dimethylisoindoles, 4,5,6,7-tetramethylisoindole[202], as well as substituted 2-methylisoindole[201], 1-methylisoindole[209], 1-azidoisoindole[203], 2-methyl-5-azaisoindole[210], 2-arylisoindole[211], and 2-(4′-pentenyl)isoindole[212] were obtained. The relevant calculations were made[190,193,200] and the ^{14}N NMR spectrum of 2-methylisoindole was measured[189,196]. The radical-cation derived from 1,3,4,7-tetramethyl-2-(4″-tolyl)isoindole was detected in the EPR spectrum[194]. Diels–Alder adducts involving isoindole derivatives[192,195,201,202,209,212,214], electrophilic reactions[213], and alkylation[197,204,207] have been studied for the isoindole series. The condensation of 1-aminoisoindole with β-diketones has been investigated[206]. The anorectic effect of substituted indoles has been observed[197,204,207]. Spectrofluorimetric methods for the determination of the lowest concentrations of aminoacids and proteins, by converting them into 1-thioisoindole derivatives, have been proposed[191,198,199,205].

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Semiconducting Pyropolymers

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Model structures which explain the electrical and the paramagnetic properties of semiconducting pyropolymers are proposed. The development of paramagnetic clusters during the formation of these polymers is demonstrated, and the generality and the thermodynamic efficiency of this process are stressed. The problems encountered when applying the theory of electrical conduction in heterogeneous materials and the theory of flows to semiconducting pyropolymers are discussed. Transport phenomena involving the charge carriers in these polymers are analysed by the theory of electronic states in disordered systems. The temperature dependence of the electrical conductivity is shown to obey Mott's law over a wide range of temperature. Quantitative relationships for the pressure dependence of the electrical parameters of powdered semiconducting pyropolymers are obtained, and the influence of the structure of these materials on their electrical and paramagnetic properties is examined. 103 references.

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I. INTRODUCTION

Many polymers showing semiconducting properties have been synthesised and investigated[1-14]. Their electrical[1-7], photoelectric[1-4,10,13,14], catalytic[1-3,15,16], and paramagnetic properties[1-3,7,16-22] have been highlighted, and the materials have been used in optical information storage systems[13,14]. The practical realisation of superconductivity with a high critical temperature by using polyconjugated polymers has been predicted[23], and though the prediction has not yet been proved correct it has made a very important contribution to the development of the physics and chemistry of molecules with conjugated bonds[16], whose photochemical and radiation-chemical stability is discussed in detail in Ref. 24.

Comprehensive theoretical studies[16,18-31] of the electronic structure and of the paramagnetism of polymers with conjugated bonds have been carried out, the properties of their molecules have been broadly characterised, and experimental observations of their optical spectra have been explained. In this context the work of Ovchinnikov[30,31] deserves special mention for combining a physical demonstration with a theoretical proof of the development of ferromagnetism in alternant organic systems. In spite of these achievements, however, a general theory of the physical properties of polymeric semiconductors is still awaited. The need for a special theory has even been questioned: as an alternative, the properties of these polymers could be described in terms of the theory of disordered systems[32-42].

In this review we shall examine from the standpoint of the theory of the electrical properties of disordered systems the relationship between the electrical conductivity (or the paramagnetism) and the structure of semiconducting pyropolymers, prepared mainly from polyacrylonitrile (PAN). The choice of these materials was dictated by the abundance of the data on the thermal transformations of PAN,[1,8,12,43-51] and by the recent publication of monographs dealing with the semiconducting properties of the PAN pyropolymers[1,2,7].

No attempt will be made to include the whole of the information on the thermal reactions of PAN and on the properties of the semiconducting products of these reactions. Published work will be mentioned only if it contains data on the structural, electrophysical, or paramagnetic properties of these materials, or if it can help to build a concrete model of the structure of semiconducting pyropolymers.

II. STRUCTURAL FEATURES AND ELECTRICAL CONDUCTIVITY OF PYROPOLYMERS

Semiconducting pyropolymers can be treated as microheterogeneous systems consisting of electrically conducting polyconjugation regions separated by barrier layers[1-3,7]. The volume fraction of the polyconjugation regions is determined by the technological conditions used in the preparation of the pyropolymer: it increases monotonically with the temperature of heat treatment, and thus it affects very markedly the interactions between these regions[52,53]. For this reason semiconducting pyropolymers prepared under different conditions cannot be described by the same type of heterogeneous model.

In order to produce a concrete model of the structure of the heterogeneous system we must first of all determine the volume fractions, the size, the types of interaction, and the distribution of the components. So far this information is available only for semiconducting pyropolymers based on PAN.[52-55]

1. Determination of the Concentration of the Polyconjugation Regions and of the Structural Parameters of Semiconducting Pyropolymers

The concentration of the components of heterogeneous semiconducting pyropolymer systems is determined by monitoring the change in an extensive factor with heat treatment temperature (T_{form}). The most convenient and easily measured extensive factor in these systems is the density, which increases with the T_{form} value of the semiconductor[53]. This suggests that the polyconjugation regions are relatively dense, and the interlayers between these regions relatively loose.

The density γ of a heterogeneous system is defined by the expression

$$\gamma = \sum_i V_i \gamma_i , \qquad (1)$$

where V_i is the volume fraction and γ_i is the density of the i-th phase. In the case of two-component systems, to which semiconducting pyropolymers can be assigned to a first

approximation, Eqn.(1) takes the form

$$\gamma = V_1\gamma_1 + (1-V_1)\gamma_2 , \qquad (2)$$

where γ_1 and γ_2 are the densities of the conducting and the non-conducting component respectively, and V_1 is the volume fraction of the polyconjugation regions. Obviously, $V_2 = 1 - V_1$ is the volume fraction of the non-conducting component. Solving Eqn.(2) for V_1 we obtain

$$V_1 = \frac{\gamma - \gamma_2}{\gamma_1 - \gamma_2} . \qquad (3)$$

In the case of PAN semiconductors the volume fraction V_1 has been determined[52,53] by formula (3) by arbitrarily identifying γ_1 with the density of the sample obtained at 1100° (assumed to consist almost exclusively of fully developed polyconjugation regions), and γ_2 with the density of the sample obtained at 200° (in which the amount of polyconjugation is negligible). This involves the assumption that the densities of the conducting and of the non-conducting component are independent of the heat-treatment temperature (T_{form}) of the sample, i.e. that only the relative amounts of the two components are affected by the pyrolysis temperature. This hypothesis is supported by studies of the frequency dependence of electrical conductivity[56] and of the frequency spectrum of the current noise[57] in pyrolysed PAN: the results confirm that the basic structure of the polyconjugation regions is unchanged by an increase in the pyrolysis temperature of the initial polymer. Though an analysis of the formation of semiconducting pyropolymers suggests[44-51] that both γ_1 and γ_2 should increase slightly with pyrolysis temperature, the inequality $\gamma_1 > \gamma > \gamma_2$ must always be satisfied, and therefore the volume fractions calculated by formula (3) cannot be greatly in error.

Table 1. Effect of the formation temperature T_{form} of PAN on the concentration of PMC, on the distance d between them, on the volume fraction V_1, the average volume $\bar{v}$, and the average linear size L of the polyconjugation regions, and on the average distance S between the "surfaces" of these regions (measurements in air)[53].

T_{form}, °C	$10^{-19}N$, spins cm^{-3}	V_1	$\bar{v}$ (Å)³	L, Å	S, Å	d, Å
300	$9.5\cdot10^{-2}$	0.07	$7.7\cdot10^{4}$	42.5	60.8	103.3
350	$3.3\cdot10^{-1}$	0.16	$5.0\cdot10^{4}$	36.9	30.7	67.5
400	1.1	0.24	$2.3\cdot10^{4}$	28.4	17.0	45.4
450	2.6	0.30	$1.2\cdot10^{4}$	22.8	11.1	33.9
500	6.7	0.38	$5.7\cdot10^{3}$	17.9	6.7	24.6
550	1.1·10	0.44	$4.0\cdot10^{3}$	15.9	4.9	20.8
600	1.5·10	0.51	$3.4\cdot10^{3}$	14.9	3.8*	18.7
650	1.7·10	0.58	$3.3\cdot10^{3}$	15.0	3.0*	18.0
700	1.3·10	0.62	$5.4\cdot10^{3}$	17.5	2.9*	20.4
750	5.1	0.72	$1.4\cdot10^{4}$	24.2	—	27.0
800	1.4·10	0.81	$5.8\cdot10^{5}$	83.4	—	89.3
850	$5.2\cdot10^{-2}$	0.85	$1.6\cdot10^{6}$	117.7	—	124.4
900	$2.1\cdot10^{-2}$	0.88	$4.1\cdot10^{6}$	161.5	—	168.3
1000	$1.5\cdot10^{-2}$	0.95	$6.3\cdot10^{6}$	185.7	—	188.7

*These values have no real physical significance.

Table 1 (taken from Ref.53) shows the volume fractions of polyconjugation regions in PAN pyropolymers, calculated by formula (3) as a function of the thermolysis temperature. The Table also shows the average effective volume corresponding to one paramagnetic centre (PMC)

$$\bar{v} = V_1/N , \qquad (4)$$

where N is the number of PMC in 1 cm^3, and the average linear size

$$L = (V_1/N)^{1/3} \qquad (5)$$

of the polyconjugation regions. On the assumption that the unpaired electrons are uniformly distributed throughout the sample, and localised on specific atoms or within their coordination sphere, we can use the expression

$$d = N^{-1/3} \qquad (6)$$

for the average distance between PMC. On the additional assumption that the distribution of polyconjugation regions over the sample is uniform and random, and using Eqns.(4) to (6), we can define an average effective distance S between the "surfaces" of the polyconjugation regions as

$$S = \frac{1 - V_1^{1/3}}{N^{1/3}} \quad \text{or} \quad S = d - L . \qquad (7)$$

Since the parameter N is affected by atmospheric oxygen, all the quantities calculated by Eqns.(4)–(7) (i.e. $\bar{v}$, L, d, and S) also depend on the conditions under which N was determined. We should note that V_1 and N (and therefore also $\bar{v}$, L, d, and S) are parameters of the structure of the semiconducting pyropolymers: the change in these parameters during the formation of the polymer reflects the growth of the polyconjugation regions in relation to the external factors. This is illustrated by the data in Table 1, from which it is clear that as the heat treatment temperature of the PAN is increased the volume fraction of the polyconjugated regions also increases to a value in excess of 50% at temperatures above 600°, and the distance between polyconjugation regions becomes shorter.

The variation of L with the thermolysis temperature of the sample yields valuable information on the growth of the polyconjugation regions during the formation of the semiconducting pyropolymers. At first sight the decrease of L with increase in heat treatment temperature (to 600°) appears inconsistent with studies of the absorption[43] and fluorescence[51] spectra of PAN at various stages of heat treatment. According to those studies more intensive thermolysis causes cross-linking of the continuous conjugation regions, reflected by a shift in the fluorescence spectrum in the near i.r. and by an increased absorption in the long-wavelength tail of the spectrum, i.e. by an increase in the length of the polyconjugation blocks. However, this apparent contradiction is easily dismissed if we consider the mechanism of thermolysis of PAN [46,51] to give polyconjugated systems with a wide distribution in size of the polyconjugation blocks[8]. Obviously, the rate of formation of these blocks (after an initial stage in the formation of the semiconducting pyropolymers) increases with the formation temperature T_{form} more rapidly than their rate of growth and coalescence, causing N to increase and L to decrease. At this stage in the heat treatment the pyropolymer is enriched in polyconjugation regions mainly through an increase in their number. On the other hand, at temperatures $T_{form} > 600°$ the polyconjugation regions can also grow and coalesce, and the number of PMC decreases (see Table 1).

Information on the electronic states of semiconducting pyropolymers and on the distribution and interaction of their components over microscopic volumes can be obtained from the ESR spectra. The ESR lines of PAN semiconductors with formation temperatures $T_{form} \leqslant 300°$, $300° < T_{form} < 600°$, and $T_{form} \geqslant 600°$ have a Gaussian, a mixed, and a Lorentzian form respectively[55]. The line width and the spin–lattice relaxation time T_1 decrease as T_{form} increases[58]. By studying samples containing different numbers of PMC a strong concentration dependence of the rate of spin–lattice relaxation was observed[58] (see Table 2), as in polyphenylacetylene

samples thermolysed at different temperatures[59,60]. This indicates exchange interaction between the PMC in thermolysed PAN for $T_{form} > 300°$, increasing with the thermolysis temperature of the polymer. We know[61] that the intensity of the exchange interaction is very sensitive to the distance between the PMC, the effect being strong at distances <10 Å. Thus we may conclude that the distance between some of the PMC in PAN pyropolymers with $T_{form} > 300°$ is less than 10 Å.

Table 2. Effect of the formation temperature T_{form} of PAN on the concentration N of PMC, on the width ΔH of the ESR line, on the average distance d between PMC, on the average number K of PMC in each cluster, and on the time T_1 (measurements in vacuum).[58]

T_{form}, °C	$10^{-19}N$, spins cm^{-3}	ΔH, Oe	d, Å	K	T_1, s
300	$9.7\cdot10^{-1}$	16	46.9	2.2	$1.1\cdot10^{-2}$
400	6.0	15	26.5	36	$3.4\cdot10^{-3}$
500	$2.0\cdot10$	4.1	17.1	238	$2.1\cdot10^{-4}$
600	$2.9\cdot10$	1.8	15.1	753	$3.9\cdot10^{-5}$

If the true distance between the PMC is calculated by formula (6) it becomes impossible to account for the observed exchange interaction, since at the maximum PMC concentration this formula gives $d \geq 18$ Å (Table 1). We must assume that in the samples prepared at $T_{form} > 300°$ the unpaired electrons are delocalised within the separate polyconjugation regions, i.e. they are π-electrons. Under these conditions the distance between the unpaired electrons of neighbouring polyconjugation regions (at the moment of nearest approach) is the quantity S, given by formula (7). But even in this case the presence of exchange interaction between the PMC in samples containing less than 5×10^{19} spins cm^{-3} cannot be accounted for. To resolve these inconsistencies we must postulate the formation of clusters (swarms) within which the distance between PMC is <10 Å in PAN pyropolymers formed at $T_{form} > 300°$: under these conditions the exchange integral becomes large. The formation of paramagnetic clusters during the preparation of semiconducting pyropolymers is a direct consequence of the local activation effect[62], which causes PMC to be formed preferentially near other PMC. The same effect has been used[63] to explain the deviation from a uniformly random distribution of the PMC in poly(vinyl chloride) samples with a modified surface.

The average number of PMC in separate paramagnetic clusters can be estimated by the method developed by Vannikov and coworkers[2,7] to determine the average number of polyconjugation regions per unit length from the current–voltage characteristic (CVC) of the sample. The method is based on the theory[64] of the CVC of heterogeneous systems consisting of layers with good and with poor electrical conductivity connected in series, the poorly conducting layers acting as barriers to the charge carriers. Ignoring the resistance of the polyconjugation regions, we can express the density j of the current flowing through the barriers as a function of the applied potential by the Petritz formula[2]

$$j = Mep\left[\exp\left(-\frac{\varphi}{k_BT}\right)\right]\left[\exp\left(\frac{e\Delta V}{k_BT}\right) - 1\right], \quad (8)$$

where p is the average concentration of the majority carriers in the polyconjugation regions, ϕ is the height of the potential barrier, ΔV is the potential step at each barrier, k_B is Boltzmann's constant, T is the absolute temperature, M is a parameter independent of ϕ and of the same order as the thermal velocity of the current carriers, and e is the electronic charge. In the low-field region we have $\Delta V \ll k_BT/e$, and Eqn.(8) becomes[2]

$$j = \frac{Mpe^2\Delta V}{k_BT}\exp\left(-\frac{\varphi}{k_BT}\right).$$

Let n_1 be the number of polyconjugation regions per unit length connected in series. The potential step ΔV then becomes[2]

$$\Delta V = V/n_1 l = E/n_1, \quad (9)$$

where V is the voltage applied to the sample, E is the field strength, and l is the thickness of the sample. In the strong field region we have $e\Delta V \gg k_BT$, and by combining (8) and (9) we obtain[2]

$$j = Mep\exp\left(-\frac{\Delta E}{k_BT}\right), \quad (10)$$

where $\Delta E = \phi - BV$, and $B = e/n_1 l$. Thus the parameter B can be obtained from the current–voltage characteristic, and used to calculate n_1.

The exchange interaction arises because of the overlap of the π-electron clouds in the polyconjugation regions responsible for the PMC clusters. In the presence of strong exchange interaction the individual PMC clusters behave as single spin-systems: within each paramagnetic cluster the barriers are practically transparent to the charge carriers, and the reistance of the cluster can be neglected in comparison to that of the layers which separate the clusters. Therefore the CBC can be used to determine effectively the number of PMC clusters per unit length. The ratio

$$k = N/n_1^3 \quad (11)$$

defines the average number of polyconjugation regions forming separate clusters, i.e. the structural parameter responsible for the mechanism of electrical conduction and of paramagnetic relaxation in these materials.

As Table 2 shows, the size of the paramagnetic clusters (characterised by the parameter k) increases with T_{form}; at the same time the spin–lattice relaxation time T_1 decreases. These results suggest that (as in the case of thermolysed polyphenylacetylene[59]) the paramagnetic relaxation occurs through the clusters. The increase in k with T_{form} also shows that in PAN semiconductors with $T_{form} < 350°$ exchange interaction occurs through nearest-neighbour PMC, whereas in samples with $T_{form} > 350°$ the interaction also involves PMC at distances much greater than the radius of the coordination sphere. This conclusion is confirmed by the gradual disappearance of the saturation effect on the ESR line as T_{form} is increased, the PAN semiconductor becoming non-saturable for $T_{form} > 600°$.[58] This observation shows that when $T_{form} > 600°$ exchange interaction between the paramagnetic clusters sets in.

The organisation of PMC into clusters during the formation of semiconducting pyropolymers enhances the degree of delocalisation of the π-electrons, and this should lead to a decrease in the internal energy of the system: in other words, cluster formation is a thermodynamically favourable process. Cluster formation of the PMC is, essentially, the first step in the formation of graphitisation nuclei, and can be treated as a self-organisation process: the formation of ordered structures in disordered systems. A recent monograph[65] is devoted to self-organisation processes in a wide variety of systems.

Thus, the above results lead to the conclusion that semiconducting pyropolymers can be treated (with adequate precision) as micro-heterogeneous, two-component, electronically

non-uniform systems consisting of regions with high and with low electrical conductivity. We can therefore attempt to apply the theory of heterogeneous materials to a description of the electrical conductivity of these polymers.

2. Theory of the Electrical Conductivity of Disordered Systems and Electrical Conductivity of Semiconducting Pyropolymers

The effective medium method has been used[66,67] in a theoretical calculation of the electrical conductivity σ of two-component (composite) systems in which one of the phases forms a matrix at all finite concentrations, and also of random mixtures in which the particles are fully disordered and do not form any regulating structure. Formulae (12) and (13) were obtained[66,67] for the matrix systems and for the random systems respectively:

$$\sigma(V_1) = \sigma_2\left[1 + \frac{V_1}{(1-V_1)/3 + \sigma_2/(\sigma_1-\sigma_2)}\right] \qquad (12)$$

$$\sigma(V_1) = \frac{(3V_1-1)\sigma_1 + (3V_2-1)\sigma_2}{4} + \left[\frac{[(3V_1-1)\sigma_1 + (3V_2-1)\sigma_2]^2}{16} + \frac{\sigma_1\sigma_2}{2}\right]^{1/2}, \qquad (13)$$

where σ_1, σ_2, V_1, and V_2 are the electrical conductivities and the volume fractions, respectively, of the conducting and of the non-conducting component of the heterogeneous system.

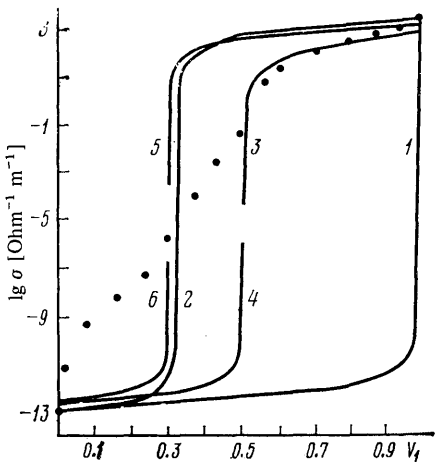


Figure 1. Electrical conductivity against volume fraction of polyconjugation regions in PAN semiconducting pyropolymers. The points are experimental, the full lines are calculated by: *1*) Eqn.(12), *2*) Eqn.(13), *3*) Eqn.(15) with $V_1 = 0.5$, *4*) Eqn.(17) with $V_c = 0.5$, *5*) Eqn.(15) with $V_c = 0.3$, *6*) Eqn.(17) with $V_c = 0.3$.

Some corrections are needed before Eqns.(12) and (13) can be used to describe the concentration dependence of the conductivity of micro-heterogeneous semiconducting pyropolymers, because these equations were derived for systems of chemically non-interacting macroscopic regions (densely compressed mixtures of particles) of high and of low conductivity. However, information on the structural details of the heterogeneous materials can be obtained from the deviation of the experimental $\sigma(V_1)$ dependence from the dependence calculated by Eqns.(12) and (13). This is illustrated in Fig.1 by curves plotted from the data of Table 1.

We note the substantial difference between the experimental $\sigma(V_1)$ plot and that calculated by formula (12) for semiconducting PAN pyropolymers. Hence, the structural model of a two-component matrix system with equally spaced inclusions of equal size, for which Eqn.(12) was derived, is not applicable to semiconducting pyropolymers. The $\sigma(V_1)$ dependence calculated by formula (13), however, is close to the experimental curve for $V_1 \geq 0.5$.

As Fig.1 shows, formula (13) predicts a critical concentration ($V_c \approx 0.333$) of the electrically conducting component at which the conductivity of the two-component system begins to rise steeply. This means that in a system with $V_1 > V_c$ we expect clusters of particles of the conducting component to permeate the whole system. Thus, Odelevskii's generalised conductivity theory[67] for random two-component mixtures implies the important concept of a critical (threshold) concentration V_c:

$$\sigma(V_c) = \frac{\sigma_2 + \sqrt{\sigma_2^2 + 8\sigma_1\sigma_2}}{4}. \qquad (14)$$

A strict mathematical definition of the threshold concentration (flow threshold), given in Ref. 68, laid the foundations of the theory of flows. A detailed analysis of the basis of this theory and of its application to the calculation of the electrical parameters of highly inhomogeneous media can be found in earlier reviews[35,36]. The flow thresholds calculated for the covalent bond problem (diamond type lattice) and for the lattice site problem (simple cubic lattice) are close to the values given by formula (13) (see Table 5.1 of Ref.36).

The following dependences have been obtained[37,38,40] by the theory of flows: for $V_1 \geq V_c$

$$\sigma(V_1) = \sigma_1(V_1 - V_c)^t \qquad (15)$$

$$\sigma(V_c) = \sigma_1(\sigma_2/\sigma_1)^s = \sigma_1 h^s; \qquad (16)$$

and for $V_1 < V_c$

$$\sigma(V_1) = \sigma_2(V_c - V_1)^{-q} = \sigma_1 h(V_c - V_1)^{-q}. \qquad (17)$$

In these expressions t, s, and q (for three-dimensional systems) have the following values[38]: $t = 1.6$, $s \approx 0.62$, and $q = t/s - t$; σ_1, V_1, and V_c are the electrical conductivity, the volume fraction, and the threshold concentration of the metallic component of the two-component system, σ_2 is the electrical conductivity of the dielectric component. If the parameter $h = \sigma_2/\sigma_1$ is very small but finite the dielectric components begin to shunt the conducting cluster when the difference $V_1 - V_c$ is small enough; under these conditions the singularity of the function $\sigma(V_1)$ at $V_1 = V_c$ disappears, and $\sigma(V_1)$ becomes a smooth function increasing monotonically from σ_2 to σ_1.[38] In the immediate vicinity of V_c Eqns. (15) and (17) are not valid, and become indistinguishable[38]. It has been suggested[37,38] that in the transition region the $\sigma(V_1)$ dependence is determined by the parameter $\Delta = h^m$ (where $m = s/t$), called the width of the transition.

Formulae (15) and (17) accurately describe the electrical conductivity of two-component systems consisting of materials with widely different conductivities. Typical examples of these systems are the cermets, and substances which undergo dielectric—metal phase transitions of the first kind at a particular temperature (for example, transition-metal oxides)[38]. The transition can be "smeared out" by inhomogeneities in the material, and extend to relatively low temperatures. As a result, a metallic phase is formed within the dielectric matrix, the volume fraction being determined (between zero and unity) by the heat treatment temperature[69].

An analogous description can be given to the formation of polyconjugation regions (the "metallic phase") in a matrix of the initial polymeric dielectric (such as PAN, poly(vinyl chloride), poly(vinyl acetate), oxidised and cross-linked polyolefins, and some resins) during heat treatment. Indeed, from the standpoint of the structure of the final product the formation of semiconducting pyropolymers and the dielectric–metal transition have a great deal in common. However, when using this analogy the essential difference in nature between these two transitions should be remembered: the phase transition is a physical transformation, but the formation of semiconducting pyropolymers is a chemical transformation. Furthermore, in metals the motion of the delocalised electrons is three-dimensional (though it may be effectively two-dimensional in very thin layers), whereas in the chains of polyconjugation blocks it is one-dimensional[27]. (The existence of one-dimensional metals has been shown[70] to be impossible.) Therefore, the problem of one-dimensional conduction in long conjugated molecular chains is still unresolved[27,39].

As Fig.1 shows, the experimental curve almost coincides with that calculated by formula (15) in the range beginning at $V_1 \cong 0.5$. Hence, for our samples[53] of heat-treated PAN we can assume $V_C \cong 0.5$, which corresponds to $T_{form} \cong 600$ °C. The reality of the high-concentration threshold predicted by the flow theory is consistent with a high level of asymmetry in the configuration of the conducting and the non-conducting regions[40].

The deviation at $V_1 < V_C$ of the experimental $\sigma(V_1)$ plot from the curve calculated by Eqn.(17) is probably due to tunnelling of the electrons through the layers of dielectric material.

We should note that the $\sigma(V_1)$ relationships calculated by Eqns.(13), (15), and (17) and $V_C \cong 0.333$ are practically identical (the width $\Delta = h^m$ of the transition between (15) and (17) is fairly small for semiconducting pyropolymers). This allows us to compare (14) and (16), which leads to the expression

$$h^s = \frac{h + \sqrt{h^2 + 8h}}{4} \quad . \tag{18}$$

The quantity s calculated by Eqn.(18) for h values between 10^{-4} and 10^{-16} lies in the range 0.57–0.51, i.e. it increases very slowly with h.

Thus, the electrical conductivity of semiconducting pyropolymers in which the volume fraction of polyconjugations ("metallic phase") regions is $V_1 > 0.5$ can be described by the theory of flows. From this we may conclude that our proposed method[53] of determining the volume fraction of polyconjugation regions correctly represents the structural features of this type of material.

Useful information on the conduction mechanism has been obtained from the temperature dependence of the conductivity in semiconducting pyropolymers[1–7,71–73]. Most of the experimental results (with a few exceptions) lie on straight-line plots of lg σ against T^{-1}. In some cases these plots include breaks. For example, a study[72] of the temperature dependence of the conductivity of thermolysed PAN samples between 1.7 and 700 K has revealed five linear regions, the activation energy for conduction decreasing with decrease of temperature. This type of change in conductivity with temperature has been discussed[74–76] in terms of the electronic theory of disordered materials[35,36].

We know[35] that the temperature dependence of hopping conduction in the constant activation energy regime is

$$\sigma = \sigma_3 \exp\left(-\frac{\varepsilon_3}{k_B T}\right) \quad . \tag{19}$$

The activation energy (ε_3) for a given temperature is defined by the differential $[d(\ln \sigma)/d(k_B T)]^{-1}$. Hence, using Mott's law

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}] \quad , \tag{20}$$

where T_0 and σ_0 are parameters of the chosen model, we find that ε_3 can be expressed as

$$\varepsilon_3 = \frac{1}{4} T_0^{1/4} k_B T^{3/4} \quad , \tag{21}$$

and therefore decreases monotonically (as $T^{3/4}$) when the temperature is lowered.

Mott[41] gives the following expressions for T_0 and σ_0:

$$T_0 = \frac{\beta}{k_B g(\mu) a^3} \quad , \tag{22}$$

$$\sigma_0 = \frac{3 e^2 \nu \Phi_0}{2} \left(\frac{g(\mu) a}{2\pi k_B T}\right)^{1/4} \quad , \tag{23}$$

where a is the radius of the localised states close to the Fermi level, $g(\mu)$ is the density of states at the Fermi level, e is the electronic charge, ν is the phonon frequency, $\Phi_0 \cong 1$ is a constant, and $\beta = 21.2 \pm 1.2$ is a coefficient calculated by the theory of flows[36].

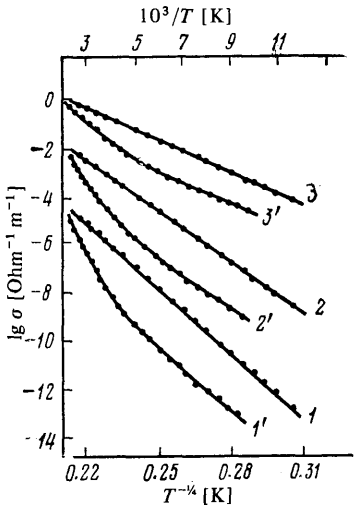


Figure 2. Temperature dependence of the electrical conductivity of PAN semiconducting pyropolymers prepared at different temperatures: *1*) and *1'*) 400°, *2*) and *2'*) 500°, *3*) and *3'*) 600°; *1*), *2*), and *3*) are in lg σ–$T^{-1/4}$ coordinates, *1'*), *2'*), and *3'*) in lg σ–T^{-1} coordinates[74].

The temperature dependence of the electrical conductivity is accurately described by straight lines (Fig.2) between 100 and 450 K when plotted as lg σ against $T^{-1/4}$, confirming that Mott's law (20) is obeyed.

Simultaneous solution of Eqns.(22) and (23) using data from Fig.2 gives unreasonable values of a and of $g(\mu)$ (see Table 3 [74]). Similar results were obtained with polyacene copolymers of the quinone radical type[77]. Therefore $g(\mu)$ was calculated by taking a as one-half of the average distance between polyconjugation regions determined by formula (7). This gave entirely reasonable values of $g(\mu)$ when Eqn.(22) was used, but calculations by Eqn.(23) gave physically

meaningless results (see Table 3). Hence, Eqn.(23) is not applicable to polymeric semiconductors. We note from Fig.2 that the temperature dependence of the conductivity is linear in lg σ against T^{-1} coordinates over relatively narrow temperature ranges, and the ε_3 values for these ranges decrease monotonically as the temperature decreases (see Table 4) [75] in accordance with Eqn.(21).

Table 3. Effect of formation temperature on the parameters of PAN samples[74].

T_{form}, °C	$10^{-4} \cdot T_0$, K	σ_{00}, Ohm^{-1}cm^{-1}	$10^{10} \cdot a^*$, cm	$g(\mu)^*$, V^{-1} cm^{-3}	$10^{9} \cdot s/2$	$g(\mu)$, eV^{-1} cm^{-3} (calc. by Ref.22)	$g(\mu)$, eV^{-1} cm^{-3}, (calc. by Ref.23)	$10^{-19} \cdot n$	$10^{-6}\mu_0$
400	$1.8 \cdot 10$	$6.1 \cdot 10^{12}$	$1 \cdot 10^{-5}$	$1 \cdot 10^{55}$	4.7	$1.3 \cdot 10^{17}$	$2.2 \cdot 10^{44}$	$1.6 \cdot 10$	$2.4 \cdot 10^{5}$
500	6.7	$5.9 \cdot 10^{10}$	$1.7 \cdot 10^{-3}$	$5.7 \cdot 10^{49}$	2 4	$2.8 \cdot 10^{18}$	$7.1 \cdot 10^{39}$	8.2	$4.5 \cdot 10^{3}$
600	1.13	$3.5 \cdot 10^{7}$	7.1	$4.8 \cdot 10^{38}$	1.3	$6.5 \cdot 10^{20}$	$2.6 \cdot 10^{33}$	3.8	5.7

*Values obtained by solving (22) and (23) simultaneously, using data from Fig.2.

Table 4. Activation energy of PAN semiconductors prepared at 400, 500, and 600° against measurement temperature [the ε_3(exper) values were obained by formula (19), the ε_3(calc) values by formula (21)].[75]

T_{form} = 400° C			T_{form} = 500° C			T_{form} = 600° C		
T, K	ε_3 (exper), eV	ε_3 (calc), eV	T, K	ε_3 (exper) eV	ε_3 (calc), eV	T, K	ε_3(exper), eV	ε_3 (calc), eV
112—124	0.165	0.159	105—113	0.120	0.114	102—108	0.072	0.077
148—162	0.190	0.191	133—147	0.140	0.137	116—126	0.083	0.082
178—194	0.223	0.219	174—190	0.170	0.167	135—151	0.093	0.093
210—232	0.257	0.249	230—264	0.215	0.210	168—188	0.110	0.109
238—280	0.282	0.280	307—425	0.280	0.282	202—232	0.125	0.127
298—431	0.364	0.361	—	—	—	270—374	0.176	0.171

The temperature dependence of the electrical conductivity of semiconducting pyropolymers reflects the structure of these materials. As stated above, pyropolymers can be treated as micro-heterogeneous systems consisting of electrically conducting polyconjugation regions separated by layers of dielectric material. The distance between the polyconjugation regions (and between their clusters) can take a set of values, since their nucleation during pyrolysis is a random process. These inhomogeneous systems can be described by Miller and Abrahams' random resistance network model[35,36], in which the polyconjugation regions are treated as the analogues of donors, and the dielectric layers as analogues of the resistance to the transfer of current carriers between donors. At low temperatures the main contribution to the conduction is that of barrier layers with low values of ε_3. On raising the temperature the contribution from layers with relatively high values of ε_3 becomes significant.

The general definition of electrical conductivity is

$$\sigma = en\mu , \qquad (24)$$

where n and μ are the concentration and the mobility of the current carriers respectively. In the case of semiconducting pyropolymer the parameter n denotes the average number of polyconjugation regions in each cluster, within which the barriers are almost transparent to the current carriers, and therefore $n < N$. Electrical conduction arises mainly from jumps of the current carriers between the polyconjugation regions and between their clusters.

In semiconductors of this type the increase in conductivity with temperature is usually ascribed to an increase in μ;[1-4,7,73] we can therefore write

$$\mu = \mu_0 \exp[-(T_0/T)^{1/4}] \qquad (25)$$

$$\sigma_0 = en\mu_0 , \qquad (26)$$

where μ_0 is a constant, independent of the measurement temperature. The n values, determined by formula (10) from the CVC, are given in Table 3 together with the μ_0 values. We see from Fig.3 that μ increases with the heat treatment temperature. Thus semiconducting pyropolymers are strongly inhomogeneous systems in which electrical conduction is by jumps of variable length over a wide range of temperature. The temperature dependence of the average jump length $\bar{r}$ is given by the expression[36]

$$\bar{r} = \frac{1}{2.73}\, a\,(T_0/T)^{1/4} .$$

The average jump length decreases as T_{form} increases (Fig.4). From Fig.3 and Table 4 we conclude that higher values of mobility correspond to higher values of the activation energy.

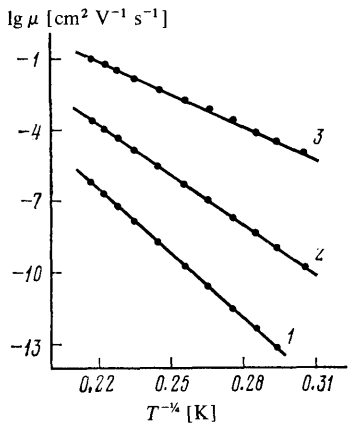


Figure 3. Temperature dependence of the mobility of the charge carriers μ in PAN semiconducting pyropolymers prepared at: *1*) 400°, *2*) 500°, and *3*) 600°.[75]

The current carriers in semiconducting pyropolymers have very low mobilities (Fig.3). Ioffe and Regel'[32-34] tried to explain the low mobilities in amorphous and in liquid semiconductors of various types, but they met some fundamental difficulties, which we shall examine below.

The mobility μ and the coresponding mean free path l of the current carriers with an effective mass m^* at room temperature are interrelated by the expression[33,34]

$$l \simeq 10^{-8} \mu (m^*/m)^{1/2} ,$$

where m is the mass of the electron. In the case of electronic semiconductors the mean free path has been shown[33,34] to lie between 10^{-9} and 10^{-4} cm. In these materials the interatomic distances are $r \cong (3-5) \times 10^{-8}$ cm, and the wave length of

the free electrons and holes moving with thermal velocity at room temperature is $\lambda \cong 7 \times 10^{-7}$ cm. It is found that $l < \lambda$ for all semiconductors with a mobility $\mu < 100$ cm^2 V^{-1} s^{-1}, and $l < r$ for $\mu < 5$ cm^2 V^{-1} s^{-1}. However, free motion of the carriers at some average velocity is possible only at a distance l. Therefore it is clear that the concept of a carrier velocity becomes meaningless for all semiconductors with $\mu < 100$ cm^2 V^{-1} s^{-1}.[33,34] As Ioffe and Regel' have pointed out, the mean free path and the mobility of the charge carriers also become meaningless for semiconductors in which $l < \lambda$ (and especially when $l < r$), since in the quantum-mechanical model the electron is "smeared out" over a region of length λ.

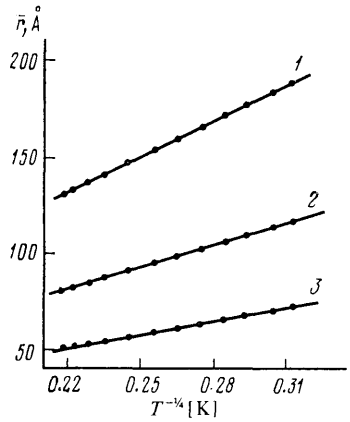


Figure 4. Temperature dependence of the average jump length of the charge carriers in PAN semiconducting pyropolymers heat treated at: *1*) 400°, *2*) 500°, and *3*) 600°.[75]

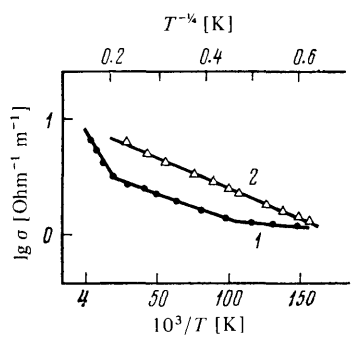


Figure 5. Temperature dependence of the electrical conductivity of a copolymer of cyano-acetylene and acetylene, plotted as: *1*) lg σ against T^{-1} (after Ref.6), and *2*) lg σ against $T^{-1/4}$.

In their treatment of the charge transport phenomenon as a special type of chemical reaction with an activation energy E Ioffe and Regel' expressed the temperature dependence of the carrier mobility (for low applied electric fields) as

$$\mu \propto \exp(-E/k_B T).$$

According to this expression the parameter μ increases exponentially with temperature in semiconductors with a low mobility of charge carriers. A low mobility, increasing with temperature, is consistent with an activational mechanism for the transfer of charge carriers through potential barriers.

The work described in Refs.32–34 laid the foundations for the development of extensive studies of the physical properties of disordered systems, such as amorphous or liquid semiconductors, in which the short-range structural order plays the key role in the formation of the electron energy spectrum and determines the localisation of the electronic states attending an increase in the structural disorder factor[42]. It has been suggested[33,34] that in low-mobility semiconductors the term "mobility" should be replaced by the concept of a frequency of transitions between localised states. The results discussed above show that an increase in temperature increases the frequency of the transition (the transition probability) of the charge carriers between the polyconjugation regions and between their clusters in semiconducting pyropolymers.

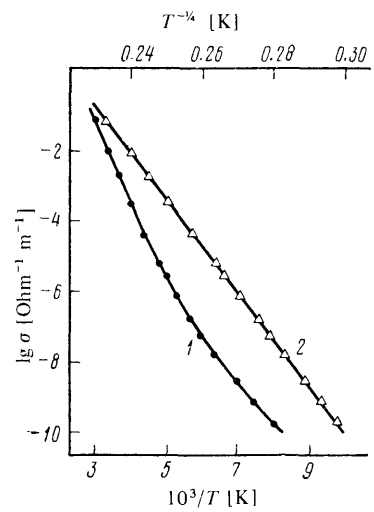


Figure 6. Temperature dependence of the electrical conductivity of thermally- and radiation-modified polyethylene, heat treated at 445° and exposed to iodine at 240°: *1*) plotted as lg σ against T^{-1}, *2*) same data, plotted as lg σ against $T^{-1/4}$.

The above interpretation of the temperature dependence of electrical conductivity applies to all semiconducting polymers. As an illustration we have plotted a large amount of published data[6,7,72,73] according to Mott's law [Eqn.(20)]. As Figs.5–8 show, the curves of electrical conductivity against temperature are linearised in many cases when plotted as lg σ against $(1/T)^{1/4}$.

We should stress that the presence of empty donors is a necessary condition for hopping conduction: in the case of semiconducting pyropolymers free sites must be available in the blocks or in the polyconjugation regions. This condition implies compensation in the semiconductor[35,36]. Hence, the report[77] that the formation of semiconducting pyropolymers is accompanied by substantial compensation appears to be correct.

In conclusion we should note that in our model the density of localised state is independent of energy. In this model the region in which Mott's law (20) applies has neither an upper nor a lower temperature limit[36]. As we see from Figs. 2 and 6–8, Mott's law is obeyed over a wide temperature range (10–600 K). Hence we may conclude that in semiconducting pyropolymers the density of states may be treated as constant over a wide temperature range.

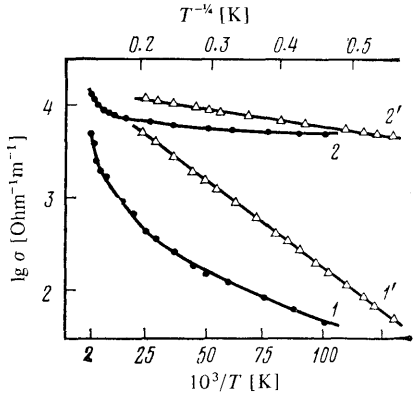


Figure 7. Temperature dependence of the electrical conductivity of PAN thermolysed at *1*) 800° and *2*) 850°: *1*) and *2*) after Ref. 72, plotted as lg σ against T^{-1}, *1'*) and *2'*) same data, plotted as lg σ against $T^{-1/4}$.

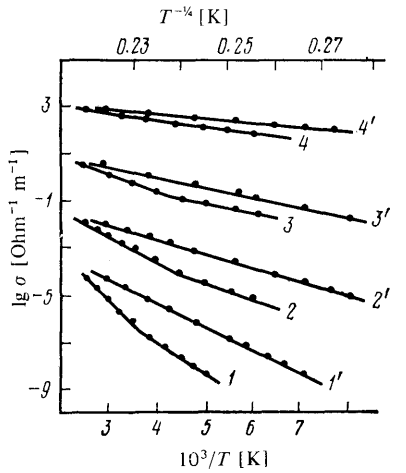


Figure 8. Temperature dependence of the electrical conductivity of PAN thermolysed at *1*) 400°, *2*) 500°, *3*) 600°, and *4*) 700°: *1*), *2*), *3*), and *4*) after Ref. 73, plotted as lg σ against T^{-1}; *1'*), *2'*), *3'*), and *4'*) same data, plotted as lg σ against $T^{-1/4}$.

Thus, from the standpoint of a concrete structural model the semiconducting pyropolymers can be divided into three groups. The first group includes the semiconducting pyropolymers in which polyconjugation regions at different distances are gradually converted (as the thermolysis temperature is increased) from isolated states into a state which can support weak exchange interactions, without formation of a joined, continuous phase. Under these conditions the Gaussian shape of the ESR line changes to a mixed shape: Lorentzian in the centre, Gaussian at the tails, and showing a saturation effect. The concentration by volume of polyconjugation regions is ~40–50% towards the upper limit of the formation temperatures of the semiconducting pyropolymers, which depends on the nature and structure of the initial component as well as on the thermolysis conditions. In the case of PAN the semiconductors prepared by thermolysis below 600° belong to the first group. According to our model the materials in this group (which have a fairly high resistance) can be treated as two-component systems in which the polyconjugation regions (or their clusters) behave as electrically conducting inclusions while the insulating component forms the continuous matrix. The distance between polyconjugation regions, i.e. the thickness of the poor conductor, has a real physical significance and determines the height of the potential barrier opposing the motion of the current carriers.

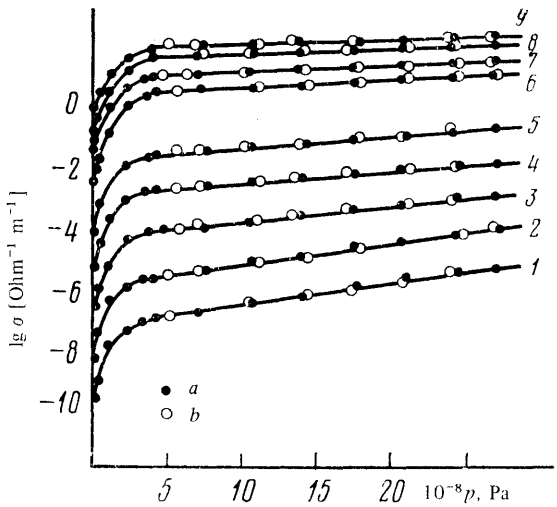


Figure 9. Electrical conductivity σ against pressure p for powdered PAN semiconductors prepared at: *1*) 400°, *2*) 450°, *3*) 500°, *4*) 550°, *5*) 600°, *6*) 650°, *7*) 700°, *8*) 750°, and *9*) 800°; (*a*) and (*b*) denote increasing and decreasing pressure runs respectively.

The second group consists of the semiconducting pyropolymers prepared at temperatures corresponding to extrema in the dependence of the number of PMC on the thermolysis temperature. The ESR line of these semiconductors is Lorentzian, and does not show a saturation effect. In the preparation of PAN semiconductors this temperature region is found between 600 and 700° (Table 1). The samples prepared at these temperatures can be described as a random mixture of a conducting and an insulating component, both components forming continuous phases. In other words, at the lower end of this range of formation temperatures the conducting component just begins to form an infinite cluster, i.e. for temperatures $T_{form} \geq 600°$ we have $V_1 > V_c$. This conclusion is confirmed by the low value of the activation energy for conduction for relatively high values of the resistivity[53]. The *S* values for these samples (denoted by an

asterisk in Table 1) are physically meaningless: they define the effective distances between polyconjugation regions for samples in which these regions are uniformly embedded in a poorly conducting matrix.

The third group includes the semiconducting pyropolymers with strong interactions between the polyconjugation regions, which occupy most of the available volume and form a continuous phase (infinite cluster). Pyropolymers of this group are formed at temperatures above the level corresponding to a decrease in the number of PMC with increase of T_{form}. Materials in this group can be treated as matrix systems, the matrix consisting of polyconjugation regions developed in three dimensions with random microscopic inclusions of a resistive component, whose volume fraction decreases as T_{form} increases. The resistive inclusions could be dielectric impurities, defects, and pores, formed during the thermolysis of the initial polymer. In these samples the distance between resistive inclusions is more meaningful than the parameter S. If the number of resistive inclusions is of the same order as the number of PMC the distance between the inclusions is of the same order as the parameter L.

We should note that the transition of semiconducting pyropolymers between these groups occurs at temperatures depending on the structure of the initial polymer and on the pyrolysis conditions. For example, inorganic substrates can lower the transition temperature of PAN semiconductors by 100–150 K.[78]

III. PRESSURE DEPENDENCE OF THE ELECTRICAL CONDUCTIVITY

If the above heterogeneous models of the structure of semiconducting pyropolymers are correct the dependence of the electrical conductivity (σ) on pressure (p) should become less marked as the pyrolysis temperature of the polymer increases, i.e. as the concentration of polyconjugation regions in the sample increases, because the latter are denser than the resistive layers between them. In other words, for the three groups of semiconducting pyropolymers defined above the pressure sensitivity should decrease in the order group I > group II > group III. This conclusion will prove correct only if the height of the potential barriers between the regions of delocalised electrons[79,80] is affected by the pressure.

Studies of the effect of pressure on the electrical conductivity of semiconducting pyropolymers are needed not only to provide an answer to this type of question but also to establish the possibility of using these materials as the sensitive element of pressure transducers, and to allow for contact phenomena between the particles of powdered samples in the measurement and interpretation of their electrical properties. The latter aspect is quite important, because many semiconducting polymers are available only as powders which cannot be pelleted. Therefore it important to know the pressure at which the powdered sample behaves as a monolithic sample, and the way to determine the electrical parameters corresponding to the monolithic state at $p \to 0$ (or at atmospheric presure), so as to obtain the electrical conductivity of individual particles of the powder.

The effect of hydrostatic compression on the electrical conductivity and thermo-electric power of PAN fibre heat-treated at 600 and 650° has been reported[79,80]. Powdered samples are thought[79] to be unsuitable for this work, because their resistance depends on contacts between particles, whereas fibres behave as monolithic specimens. However, fibres cannot be used to study carrier transport over a wide range of pressure, because they break at loads >8 kbar.[1] We have therefore studied[81,82] the effect of quasi-hydrostatic pressures between atmospheric and 30 kbar on the electrical conductivity parameters of powdered semiconducting pyropolymers based on PAN and thermolysed at 300–900°. This work has produced convincing answers to some of the questions formulated above, and will be reviewed in some detail.

In Fig.9, taken from Ref.82, two regions can be distinguished: in the first σ rises very steeply as p is raised to 3.4×10^8 Pa, suggesting densification of the powdered sample and an increase in the area of contact between the particles. We know[83] that the average porosity of a compressed powder decreases monotonically as a function of the applied pressure, and vanishes at a specific pressure, when the density and the conductivity of the sample become equal to those of the individual particles of the power. We see from Fig.9 that for heat-treated PAN powders this pressure lies in the region of 3500–4000 kg cm^{-2}. Beyond these pressures we observe the second region, in which the experimental points (plotted as lg σ against p) are almost indistinguishable from the straight lines

$$\sigma = \sigma_{p=0} \exp\left(\frac{ap}{k_B T}\right), \qquad (27)$$

where a is a constant.

Table 5. Dependence of $\sigma_{p=0}$ and of the parameter a on the heat treatment temperature (T_{form}) of PAN.[82]

T_{form}, °C	$\sigma_{p=0}$, Ohm^{-1} cm^{-1}	$10^{-4}a$, eV cm^2 kg^{-1}	T_{form}, °C	$\sigma_{p=0}$, Ohm^{-1} cm^{-1}	$10^{-4}a$, eV cm^2 kg^{-1}
400	$3.97 \cdot 10^{-10}$	4.2	650	$3.97 \cdot 10^{-3}$	1.1
450	$1.41 \cdot 10^{-8}$	3.68	700	$1.58 \cdot 10^{-1}$	0.9
500	$6.25 \cdot 10^{-7}$	2.65	750	$8.85 \cdot 10^{-1}$	0.6
550	$1.77 \cdot 10^{-5}$	1.84	800	1.77	0.36
600	$2.94 \cdot 10^{-5}$	1.69			

The pre-exponential term $\sigma_{p=0}$ for a monolithic sample corresponds to the electrical conductivity in the absence of pressure[79]. In the case of a powdered sample $\sigma_{p=0}$ defines the electrical conductivity at zero pressure but assumed independent of the contact between the particles, i.e. $\sigma_{p=0}$ corresponds to the monolithic state of the powder at $p = 0$. The true value of $\sigma_{p=0}$ for a powder is determined by extrapolating to $p = 0$ the linear portion of the lg σ against p plot. Values of $\sigma_{p=0}$ obtained in this way and values of a calculated by Eqn.(27) for PAN samples heat-treated at different temperatures are given in Table 5 (taken from Ref.82). As T_{form} is increased the constant a decreases, and $\sigma_{p=0}$ increases. This quantity is identical to the value $\sigma_{20°}$ obtained from the plots of lg σ against T^{-1} at a pressure of 3500 kg cm^{-2}. Hence, and in the light of the above definition of $\sigma_{p=0}$, we can write

$$\sigma_{p=0} = \sigma_3 \exp\left(-\frac{\varepsilon_3}{k_B T}\right), \qquad (28)$$

where ε_3 is the thermal activation energy for conduction at zero pressure. Thus Eqn.(28) describes the temperature dependence of the hopping conduction in the constant activation energy regime at zero pressure.

From formulae (27) and (28) we obtain the following expression for the temperature dependence of the electrical conductivity in the presence of an applied pressure:

$$\sigma = \sigma_3 \exp\left(-\frac{\varepsilon_3 - ap}{k_B T}\right). \qquad (29)$$

It follows from this expression that a is a quantity (depending on the nature of the sample) which describes the decrease in the activation energy for electrical conduction in semiconducting pyropolymers brought about by the application of unit pressure, i.e.

$$\varepsilon_3'-\varepsilon_3''=-a(p_1-p_2) \quad \text{or} \quad \Delta\varepsilon=-a\Delta p\,, \tag{30}$$

where ε_3' and ε_3'' are the activation energies for conduction at pressures p_1 and p_2 respectively. As Table 6 shows[82], the activation energy for conduction decreases linearly with increase of pressure, as required by Eqn.(30). Extrapolation to zero pressure gives the activation energy for conduction in the "monolithic" state of the powder in the absence of pressure. The activation energies for conduction obtained in this way are 0.01–0.02 eV lower than the values for powder samples densified by vibration.

Table 6. Electrical conductivity parameters of heat-treated PAN at different pressures.

$10^3\,p$, kg cm^{-2}	T_{form} = 400 °C			T_{form} = 550 °C			T_{form} = 700 °C		
	$\sigma_{20°C}$, Ohm^{-1} cm^{-1}	σ_{ε_a}, Ohm^{-1}cm^{-1}	ε_a, eV	$\sigma_{20°C}$, Ohm^{-1}cm^{-1}	σ_{ε_a}, Ohm^{-1}cm^{-1}	ε_a, eV	$\sigma_{20°C}$, Ohm^{-1}cm^{-1}	σ_{ε_a}, Ohm^{-1} cm^{-1}	ε_a, eV
0.001*	$1.41\cdot10^{-12}$	$7.80\cdot10^{-6}$	0.39	$4.17\cdot10^{-8}$	$1.33\cdot10^{-3}$	0.26	$3.57\cdot10^{-4}$	$6.3\cdot10^{-2}$	0.13
4.00	$7.04\cdot10^{-10}$	$1.76\cdot10^{-3}$	0.37	$2.24\cdot10^{-5}$	$4.7\cdot10^{-1}$	0.25	$1.77\cdot10^{-1}$	14.1	0.11
10.80	$2.32\cdot10^{-9}$	$1.82\cdot10^{-3}$	0.34	$4.17\cdot10^{-5}$	$3.94\cdot10^{-1}$	0.23	$2.24\cdot10^{-1}$	12.0	0.10
18.00	$7.61\cdot10^{-9}$	$1.74\cdot10^{-3}$	0.31	$6.10\cdot10^{-5}$	$3.84\cdot10^{-1}$	0.22	—	—	—
21.40	$1.26\cdot10^{-8}$	$1.95\cdot10^{-3}$	0.30	$8.9\cdot10^{-5}$	$3.80\cdot10^{-1}$	0.21	$3.71\cdot10^{-1}$	13.4	0.09

*These data refer to a powder densified by vibration in a quartz cylinder at atmospheric pressure.

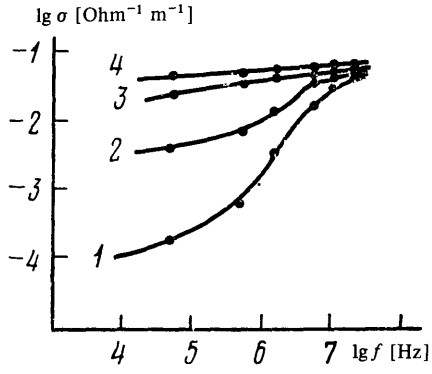


Figure 10. A.c. conductivity against frequency at different pressures for a sample of PAN heat treated at 600°: *1*) atmospheric pressure, *2*) 1.0×10^3, *3*) 3.5×10^3, *4*) 1×10^4 kg cm^{-2}.[82]

We would stress that in the linear region of the plots of lg σ against p the change of σ with pressure is reversible (see Fig.9), and therefore in this region (at $p \geq 3500$ kg cm^{-2}) the properties of the powdered semiconducting pyropolymer samples are indistinguishable from those of monolithic specimens. Measurements of the a.c. conductivity under pressure have confirmed this view. Since the conductivity of a fibre (monolithic specimen) of thermolysed PAN is independent of frequency[79], the gradual decrease in the frequency dependence of conductivity with increase of pressure (Fig.10) confirms the above conclusion.

In 1960 Tal'roze and Blyumenfel'd[84] observed a linear dependence of lg σ_3 on ε_3 (i.e. a compensation effect) in a wide range of polymeric semiconductors. A detailed analysis of various aspects of this phenomenon from the point of view of the chemical physics of the solid state is given in Ref.85. As Fig.11 shows, a linear relationship is observed also between lg $\sigma_{p=0}$ and a, which vary in opposite senses, i.e. according to the equation

$$a=b+c\lg\sigma_{p=0} \tag{31}$$

whose coefficients b and c (calculated by least squares) are 0.456×10^{-6} and -0.382×10^{-6} respectively.

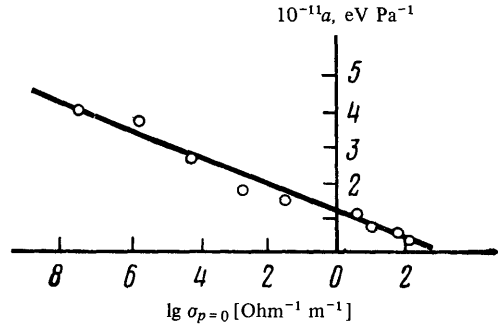


Figure 11. Pre-exponential factor $\sigma_{p=0}$ in Eqn.(27) against the constant a for heat-treated PAN samples[82].

From the lack of dependence of the pre-exponential factor σ_3 on p in the linear part of the lg $\sigma(p)$ function (see Fig.9 and Table 6) and from the inverse variation (31) between $\sigma_{p=0}$ and a we may conclude that the main effect of pressure is an increase in the mobility of the charge carriers, the concentration of the carriers being unaffected by the pressure. The same conclusion was reached[80] from an observation of the pressure-independence of the thermo-electric power of pyrolysed PAN fibre, coupled with a decrease in the activation energy for electrical conduction with increase of pressure.

However, we should point out that Shimamura and coworkers[86,87] concluded from a study of the electrical conductivity of polyacetylene at pressures up to 108 kbar between room temperature and liquid-nitrogen temperature that the concentration of current carriers increases with pressure. This conclusion is incorrect, because the pre-exponential factor is sensitive to changes in the density of charge carriers[4], and therefore constancy of this factor coupled with a decrease in the activation energy for conduction with increase of pressure implies that the main influence of pressure on the electrical conductivity of polymeric semiconductors is to increase the mobility of the carriers by lowering the potential barriers.

From Tables 5 and 6 and Fig.9 we note that the pressure dependence of the electrical conductivity decreases as T_{form} increases, i.e. as the volume concentration of polyconjugation regions increases. These results indicate that the structural features of the pyropolymers and their changes with thermolysis temperature are correctly reflected, on the whole, by the heterogeneous models discussed above. They also show that the main effect of pressure is on the potential

barriers which separate the regions containing delocalised electrons. In other words, the insulating inter-layers are more compressible than the polyconjugation regions. The semiconducting pyropolymers of group I are the more pressure-sensitive, and they can be used as the sensing element in pressure transducers. A detailed analysis of the advantages of polymeric semiconductors as materials for pressure transducers will be found in Ref.88.

IV. RELATIONSHIP BETWEEN THE NUMBER OF PARAMAGNETIC CENTRES AND THE ELECTRICAL CONDUCTIVITY

A large volume of work, reviewed in Refs.1, 2, and 7, suggests the existence of a definite relationship between the electrical and the paramagnetic properties of polymeric semiconductors. However, different points of view have been put forward in the interpretation of this phenomenon. For example, some workers[89,90] consider that at high enough levels of conjugation (i.e. under conditions of eka-conjugation) the electronically excited state can exist at room temperature because the distance between the ground and the triplet state is small, and charge carriers formed by the scheme

$$R + \ddot{R} \rightleftarrows R^+ + R^-$$

are recorded in the ESR spectra. The authors[89,90] used the theory of rate processes to explain the relationship between conductivity and paramagnetism in polymers with conjugated bonds.

Vlasova and coworkers[91,92] conclude from the good agreement between experimental values of the thermoelectric power of thermolysed PAN and polypyridine and the values calculated by the band theory of solids that the PMC behave as donor impurities in these materials. This work suggests (implicitly) that the unpaired electrons transferred to the conduction band by the ionisation of the donors give the same ESR signal as the electrons still in the filled donors[2]. Further work is needed to confirm this conclusion.

An analysis of the electrical and paramagnetic characteristics of polymeric semiconductors led Vannikov and Boguslavskii[2] to conclude that in most cases a direct link between the electronic states which control the electrical and the paramagnetic properties cannot be established. If such a link exists, it can only be discovered by detailed studies and comparisons of the electrical and paramagnetic properties over a wide range of experimental conditions and of chemical composition and structure of the sample[2]. We note in this connection the work of Volod'ko and coworkers[93], who obtained an expression directly relating the electrical conductivity and the number of PMC by using the hopping model of conduction. According to that model the mobility is expressed by the formula[4]

$$\mu = \frac{fSeN_s(k_BT)}{h^2\nu^2}\exp\left(-\frac{\varepsilon_s}{k_BT}\right), \qquad (32)$$

where f is the average angle between the jump direction and the vector of the electric field, S is the distance between molecules, N_S is the number of neighbouring molecules, ν is the vibration frequency of the activated complex in a plane normal to the direction of motion of the charge carriers, ε_S is the height of the barrier, and h is Planck's constant. In the case of semiconducting pyropolymer S is interpreted as the distance between polyconjugation regions, and N_S as the number of adjacent polyconjugation regions.

Eqn.(32) has no practical applications, because it contains quantities which cannot be measured experimentally. Therefore, introducing the substitutions

$$S=\xi_1 N^{-1/3};\ f=a_0N^{1/3}/\xi_1;\ N_s=R^3N;\ \varepsilon_s=\varepsilon_3;\ \nu=\varepsilon/\hbar;\ n=N\xi, \qquad (33)$$

where a_0 is the mean radius of the molecule, R is the mean intermolecular interaction radius, ξ is a quantity depending on N, ξ_1 is a constant, and ε_3 is the activation energy for hopping conduction, Volod'ko and coworkers[93] obtained from (24) and (32) the expression

$$\sigma=\alpha_1\varphi(N)N^{5/3}(k_BT/\varepsilon_3)^2\exp\left(-\frac{\varepsilon_3}{k_BT}\right), \qquad (34)$$

where $\phi(N)$ is a function of N, and

$$\alpha_1=e^2a_0\xi_1R^3/\hbar. \qquad (35)$$

Formula (34) accurately describes the electrical conductivity of polymers with a polyconjugated system if the following condition applies[93]:

$$\varphi(N)=\varphi_0\exp\left(-\beta\frac{N^{1/3}}{\gamma+N^{1/3}}\right). \qquad (36)$$

Inserting (36) into (34) gives

$$\sigma=\alpha N^{5/3}\left(\frac{k_BT}{\varepsilon_3}\right)^2\exp\left[-\frac{\varepsilon_3}{k_BT}-\beta\frac{N^{1/3}}{\gamma+N^{1/3}}\right], \qquad (37)$$

where $\alpha = \alpha_1\phi_0$, β, and γ are constants; the values $\ln\alpha = -44.7$, $\beta = 40$, and $\gamma = 1.3\times10^6$ were obtained[93] by least squares.

Satisfactory agreement was obtained in a comparison[93] of experimental electrical conductivity data for 44 polymeric semiconductors with the values calculated by formula (37). Differences of an order of magnitude between calculated and experimental conductivities are ascribed to errors in the measurement of the activation energy for conduction and of the concentration of PMC. However, in some samples discrepancies as high as 1.4–7 orders of magnitude were obtained[93]: no attempt was made to explain these large errors.

In spite of the satisfactory results given by formula (37) for most of the materials studied by Volod'ko and coworkers[93], the extent to which this formula is universal remains to be established. To solve this problem we need first of all to demonstrate the universality of the constants α, β, and γ which appear in formula (37), and the lack of dependence of the results upon the type of interaction between the PMC.

Comparing the first of the substitutions (33) with Eqn.(7) we can write, for the case of semiconducting pyropolymers,

$$\xi_1=1-V_1^{1/3}=1-LN^{1/3}, \qquad (38)$$

i.e. ξ is the linear fraction of dielectric inter-layers between polyconjugation regions. Inserting (38) into (35) we obtain

$$\alpha=\frac{e^2a_0(1-V_1^{1/3})R^3}{\hbar}\varphi_0=\frac{e^2a_0(1-LN^{1/3})R^3}{\hbar}\varphi_0. \qquad (39)$$

In the case of semiconducting pyropolymers a_0 and R are interpreted as $L/2$ and $S/2$ respectively, i.e. within the definition of the structure parameters given in Section II $a_0 = L/2$ and $R = S/2$. Hence, when applied to semiconducting pyropolymers Eqn.(39) becomes

$$\alpha=\frac{e^2L(1-V_1^{1/3})S^3}{16\hbar}\varphi_0. \qquad (40)$$

Clearly, the quantity α depends on the nature and on the structure parameters of the polymeric semiconductor, i.e. it takes a different value for each polymer. Therefore the use[93] of a single value (ln

($\ln\alpha = -44.7$) to calculate the electrical conductivity of polymeric semiconductors by Eqn.(37) is unjustified. This is

probably one of the main reasons for the discrepancy between experimental conductivities and those calculated by Eqn.(37). Nothing has been said about the universality of the constants β and γ, since there is no physical justification for the choice of the function (36), which appears to have been purely empirical. Nevertheless this function shows how complex is the relationship between the concentration and mobility of the charge carriers and the number of PMC in the polymer.

The reason why formula (37) with the constants α, β, and γ given in Ref.93 can be used for semiconducting pyropolymers according to the nature of the interactions between PMC was discussed in Ref.54. It was shown that the electrical conductivity of semiconducting pyropolymers of group I (see Section II), in which the polyconjugation regions and their clusters do not merge into a continuous phase, i.e. in which the interaction between these regions are weak, are most accurately described by formula (37). The largest deviations occur with samples from group II, prepared at temperatures corresponding to extrema in the dependence of the number of PMC on the thermolysis temperature of the initial polymer. The same conclusion follows from Eqn.(40), since in semiconductors of groups II and III the parameter S has no real physical meaning (see Section II).

To conclude this Section we should stress the following aspect. By comparing Eqn.(29) for $p = 0$ with Eqn.(37) we obtain

$$\sigma_3 = \alpha N^{2/3} \left(\frac{k_B T}{e_3}\right)^2 \exp\left(-\frac{\beta N^{1/3}}{\gamma + N^{1/3}}\right) . \qquad (41)$$

Though this comparison of the universal (over a narrow temperature range) equation (29) at $p = 0$ with an expression [Eqn.(37)] whose universality remains to be proved is not entirely justified, it nevertheless allows us to highlight some special features of the quantities ϕ_3, α, β, and γ. Eqn.(41) relates the pre-exponential factor ϕ_3 (which appears in formula (19) for the hopping conductivity in the constant activation energy regime) to the number of PMC. Hence, the relationship between the electrical conduction and the paramagnetic characteristics of semiconducting pyropolymers takes place mainly through the parameter ϕ_3.

We have shown (see Section III) that in the region of reversible pressure effects on the conductivity the pre-exponential factor ϕ_3 in Eqn.(29) is independent of pressure. From this we may conclude that the effects of pressure on the quantities which appear in Eqn.(41) must be mutually compensating. The activation energy for conduction decreases as the pressure increases, in accordance with Eqn.(30). It is evident from Eqn.(40) that the quantity α also should decrease with pressure, since it is proportional to S^3, where S is the thickness of the resistive layers between polyconjugation regions, to which the pressure is effectively applied. The changes in α and in ε_3 brought about by pressure may largely cancel out. A change of N with pressure seems unlikely in the region of reversible pressure dependence of the electrical conductivity of semiconducting pyropolymers. Therefore we are led to the conclusion that β and γ are unaffected by pressure, or that their pressure changes are mutually compensating.

V. CONCLUSIONS

Research into the preparation, properties, and applications of micro-heterogeneous semiconducting pyropolymers may develop in a number of new directions. The structural models of these polymers discussed above suggest the possibility of modifying their properties merely by controlling the degree of interaction between the polyconjugation regions in the system. The gradual change in properties of the initial polymer caused by increasing the thermolysis temperature can be classified as a thermal modification process. However, controlled changes in the properties of semiconducting pyropolymers by the addition of various compounds are also possible. For example, the controlled modification of the paramagnetic and of the adsorption properties of PAN semiconductor pyropolymers by doping with anthracene has been demonstrated[94-96]. The effect of additions of nickel during the pyrolysis of PAN on the electrical properties of the product has been investigated[97,98]. Metal-containing polymeric semiconductors of this type are potentially interesting as selective catalysts based on polyconjugated matrices, and also as materials for switching applications.

We believe that one of the most promising new developments will be the modification of fillers by semiconducting pyropolymers. This area of work includes methods of controlling the grafted polymerisation of acrylonitrile, vinyl acetate, and vinyl chloride on the surface of ordinary cheap fillers. Heat treatment of fillers modified in this way should give electrically conducting fillers for plastics with entirely new properties[99-103]. The work must include a study of the formation of semiconducting pyropolymers on the surface of cheap mineral filler particles, and of the effect of the fillers modified in this way on the physicochemical properties of the polymeric binders. All these problems need to be studied in detail.

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Metal Ions in Unusual and Unstable States of Oxidation and the Steps of Electrochemical Reactions

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Problems associated with the steps of electrochemical discharge and ionisation reactions of metals in aqueous solutions are discussed. Data on the radiation-chemical preparation of metals in unusual and unstable states of oxidation are reported. The results of studies of the physicochemical properties of these species in aqueous solutions and of their reactions with organic and with inorganic compounds are generalised. The effect of metal ions in unusual and unstable states of oxidation on the elementary steps of electrode reactions is discussed. 162 references.

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I. INTRODUCTION

It is generally assumed[1-3] that complex electrochemical oxidation–reduction reactions consist of several elementary (one-electron) electrochemical acts. The intermediate steps of these reactions (for example, the anodic dissolution or the cathodic deposition of metals) give ions in unusual and unstable states of oxidation. Since the direct experimental observation of these short-lived intermediate species is impossible at present, any conclusion as to the steps involved in an electrochemical reaction must be based on an analysis of the kinetics of the process. However, the criteria used to identify the steps cannot usually yield an unambiguous description of the overall mechanism of the process. Nevertheless metal ions in unstable states of oxidation have been obtained by radiation-chemical methods (mainly in aqueous solutions), and their properties have been studied in fair detail. It could be useful to review and discuss these results from the standpoint of a more fundamental understanding of the mechanism of the multi-step discharge and ionisation reactions of metals.

II. STEP REACTIONS IN ELECTROCHEMICAL KINETICS

The theory of multi-step electrode processes is based on the proposition that the transfer of several electrons in a single elementary discharge (or metal ionisation) act is less probable than the sequential transfer through one-electron intermediate steps. Thus a multi-step electrochemical reaction presupposes the formation of metal ions having intermediate valencies.

The fullest discussion of multi-step electrochemical processes can be found in papers[4,5] describing the anodic dissolution of iron in alkaline solutions by the overall reaction

$$Fe + 2OH^- \rightleftarrows Fe(OH)_2 + 2e .$$

The experimental results were explained by postulating the formation (in a one-electron process) of the intermediate surface compound Fe(OH)(ads):

$$Fe + OH^- \rightleftarrows Fe(OH)(ads) + e$$

followed by the slow step

$$Fe(OH)(ads) + OH^- \rightarrow FeO(ads) + H_2O + e$$

and by the fast reactions leading to the formation of the final product

$$FeO(ads) + OH^- \rightleftarrows HFeO_2^- ,$$
$$HFeO_2^- + H_2O \rightleftarrows Fe(OH)_2 + OH^- .$$

The mechanism of a multi-step electrode process on a solid electrode is difficult to study because of the imperfection of real surfaces, and also because the electrochemical discharge (ionisation) reaction is often accompanied by other steps such as diffusion of the species being discharged to crystallisation sites, their incorporation into the lattice, etc. The amalgam electrode is more convenient for theoretical and experimental studies of step reaction mechanisms, and it offers some important advantages over solid electrodes. We shall therefore confine this discussion mainly to data obtained for multi-step electrode processes on amalgams.

1. Criteria of Step Mechanism

The recognition of a step mechanism in an electrochemical reaction is usually based on an analysis of the reaction kinetics. Theoretical rules developed for this purpose[2,3,6-9] have been called the "criteria of step mechanism": they are discussed in detail in Ref. 3.

The step mechanism of a complex electrochemical reaction can be demonstrated by studying the kinetics of the cathodic and of the anodic process. Consider the overall discharge (metal ionisation) reaction

$$M \rightleftarrows M^{n+} + ne \qquad (1)$$

whose rate is limited by the slow step

$$M^{(m-1)+} \underset{k_{cm}}{\overset{k_{am}}{\rightleftarrows}} M^{m+} + e . \qquad (2)$$

According to the slow discharge theory[10], the rates of the anodic and of the cathodic process are given by

$$i_{am} = k_{am}[M^{(m-1)+}]_s \exp\left(\frac{\beta_m F(\varphi - \psi_1)}{RT}\right) , \qquad (3)$$

$$i_{cm} = k_{cm}[M^{m+}]_s \exp\left(-\frac{\alpha_m F(\varphi - \psi_1)}{RT}\right) , \qquad (4)$$

where ψ_1 is the potential at a point one ionic radius away from the electrode surface measured from the potential in the volume of the solution, and α_m and β_m are the true transfer coefficients of the m-th step, for which we can write

$$\alpha_m + \beta_m = 1 . \qquad (5)$$

By using the Nernst equation we can determine the concentrations of intermediate species $M^{(m-1)+}$ and M^{m+}, and thus we can replace Eqns.(3) and (4) (using the subscripts s and v to denote surface and volume concentrations respectively) by

$$i_{am} = k_{am}[M^{(m-1)+}]_v \exp\left(\frac{\beta_m F\varphi}{RT}\right) \exp\left[-\frac{(m-1+\beta_m)F\psi_1}{RT}\right] , \qquad (6)$$

$$i_{cm} = k_{cm}[M^{m+}]_v \exp\left(-\frac{\alpha_m F\varphi}{RT}\right) \exp\left[-\frac{(m-\alpha_m)F\psi_1}{RT}\right] . \qquad (7)$$

The apparent transfer coefficients of the anodic (β) and of the cathodic (α) process are related to the true coefficients β_m and α_m by the expressions

$$\begin{gathered}\beta = m - 1 + \beta_m , \\ \alpha = n - m + \alpha_m , \\ \alpha + \beta = n .\end{gathered} \qquad (8)$$

The criteria for the presence of steps can be formulated by analysing the kinetic features of the electrode process. In the case of a single rate-limiting step the criterion for a step mechanism is the dependence of the ratio of the apparent transfer coefficients (defined by the slopes of the anodic and the cathodic curve) on the number m of the limiting step:

$$\beta/\alpha = (m - 1 + \beta_m)/(n - m + \alpha_m) \qquad (9)$$

and also the fact that the sum of these coefficients is equal to the total number of electrons taking part in reaction (1) [as required by Eqn.(8)].

If in a two-step process the first step is rate-limiting, and the second is a disproportionation reaction, the kinetic equations for the cathodic and the anodic process will be the same as for one-electron reactions. Lastly, if successive steps in a process have comparable rates we observe a discrepancy between the sum of the apparent transfer coefficients and the total number of electrons taking part in the reaction (i.e. $\alpha + \beta < 2$). In this case the most important criteria for a step mechanism are the difference between the exchange currents obtained from the anodic and the cathodic Tafel plot and the difference between the true and the extrapolated value of the exchange current.

The methods of analysing polarisation curves in order to identify the step mechanism of electrochemical processes have been improved. Thus, a computer-aided approach to the analysis of the transition regions of polarisation curves has been developed[11] for studies of fast electrode reactions. Characteristic changes in shape have been established also for the differential curves in the case of a simple one-step process or for two consecutive processes having comparable rates. These changes are found to be adequate criteria for the recognition of step mechanisms.

2. Step Reactions

We shall illustrate the application of the step mechanism criteria to the study of electrochemical processes, and the demonstration of the participation (as intermediates) of metals in unusual states of oxidation, by examining briefly a few specific examples. Studies of the polarisation curves of a labelled zinc amalgam (0.4 M) in 0.1 M $ZnSO_4$ + 0.01 N H_2SO_4 have shown[12,13] that the sum of the apparent transfer coefficients at potentials close to the equilibrium value is approximately 2, and their ratio is approximately 1.6. Similar results were obtained for an indium amalgam in the presence of an excess of $NaClO_4$ [14,15] (found, $\alpha + \beta \cong 3.1$ and $\beta/\alpha \cong 2.4$). It follows from the step mechanism criteria that in both cases we are dealing with a complex electrochemical process in which the rate-limiting step is the removal of the last electron (for the anodic process) or the

addition of the first electron (for the cathodic process), i.e. the results are consistent with the electrochemical formation and with the existence of the ions Zn^+ and In^{2+} in aqueous solutions.

Published data (reviewed in Refs.1–3) clearly show that a substantial difference between the apparent transfer coefficients of the anodic and of the cathodic process is a common feature of all multi-electron discharge (metal ionisation) processes: as a rule, $\beta > \alpha$. For example, for cadmium amalgams β is 1.36–1.78 [16–19] and α lies in the range 0.24–0.28 [20,21], for copper amalgam $\beta = 1.60$ and $\alpha = 0.41$,[22] and for gallium, tin, and lead amalgams α values of 0.23,[23] 0.4–0.6,[24] and 0.5 [25] have been reported, with $\beta = 1.3$–1.6.

An example of a stepwise redox reaction with two consecutive steps taking place at comparable rates is

$$Tl^+ \rightleftarrows Tl^{3+} + 2e\,.$$

The kinetics of this reaction in 15 *N* H_2SO_4 have been studied on a platinum electrode: after being corrected for diffusion the polarisation curves show linear regions corresponding to $\beta = 0.64$ and $\alpha = 0.36$, i.e. $\alpha + \beta < 2$.[26] Extrapolation of these regions to the equilibrium potential gives very different exchange currents, indicating the presence of one-electron ionisation reactions having comparable speeds:

$$Tl^+ \rightleftarrows Tl^{2+} + e\,,$$
$$Tl^{2+} \rightleftarrows Tl^{3+} + e\,.$$

Similar results have been reported for polarisation measurements in the $Pb^{2+} \rightleftharpoons PbO_2 + 2e$ system in concentrated solutions of $HClO_4$.[27] Here $\alpha = 0.86$, $\beta = 0.24$, and the exchange current found by extrapolating the Tafel portion of the anodic branch of the polarisation curve is higher than the exchange current given by the cathodic branch. These results can be explained by postulating the formation of tervalent lead in an intermediate step of the electrochemical process.

The rate of discharge (or ionisation) of many metals is a sensitive function of pH. One possible explanation assumes that the electrode process is stepwise, and that the rates of the various steps are affected to different extents by the concentration of H^+ ions. Exactly the same explanation has been proposed for the decrease in the rate of the electrode process with increase in the acidity of the medium in the case of an indium amalgam[28,29]. The rate-limiting step does not involve simple In^{2+} ions, but ions which have been partially hydrolysed,

$$InOH^+ \rightleftarrows InOH^{2+} + e\,,$$

this reaction being preceded by the hydrolysis step

$$In^{2+} + H_2O \rightleftarrows InOH^+ + H^+$$

and followed by the chemical step

$$InOH^{2+} + H^+ \rightleftarrows In^{3+} + H_2O\,.$$

The difference in rate between the anodic and the cathodic discharge (or ionisation) of bismuth has also been explained by postulating a step mechanism and by allowing for the hydrolysis of bismuth in intermediate states of valency[30]. The rate of the electrode reactions is affected also by the nature and concentration of the anions present in solution, suggesting complex formation during the intermediate steps of the electrode process, anion effects on the electron transfer conditions, or adsorption of the anions on the electrode[29].

The strongly inhibiting effect of surface-active substances (SAS) on the discharge (or ionisation) of multivalent metals (as compared with the corresponding effect on univalent metals) has been known for a long time[31,32]. This is another indication of a step mechanism, the various steps being affected by the SAS to different extents. The kinetics of electrode processes on a tin amalgam in the presence of camphor (SAS) have been studied in detail[33–35]. Evaluation of the polarisation and adsorption measurements on a computer showed that camphor causes a ~70-fold decrease in the rate of the redox step

$$Sn^+ \rightleftarrows Sn^{2+} + e\,,$$

whereas the rates of formation and of discharge of the singly charged cations,

$$Sn \rightleftarrows Sn^+ + e\,,$$

are decreased only 5-fold. The difference in the effects of the SAS on the different steps is due to the difference in nature of these steps and to the differences in hydration energy of the various steps.

A retardation by SAS in various potential regions (corresponding to different rate-limiting steps) has been observed in a study of the stepwise discharge (ionisation) of bismuth on an amalgam electrode in the presence of hydroquinone[36]. A study of the discharge (ionisation) mechanism of copper[37–39] has revealed the two sequential steps

$$Cu \rightarrow Cu^+ + e\,,$$
$$Cu^{2+} + e \rightharpoonup Cu^+\,.$$

The rate of both these steps is affected by the nature of the solvent (aqueous 2M $HClO_4$ solution, CH_3OH, or glacial acetic acid).

We should stress that the stepwise mechanism criteria are not unambiguous, because they are often based on a large number of assumptions (that the one-electron steps are first-order reactions, and purely electrochemical, i.e. that no additional chemical steps are present; also, that parallel electrochemical reactions are absent, that specific adsorption of the initial, intermediate, and final products is negligible, and that diffusional rate limitation can be ignored). Hence it is very important to establish additional criteria and other methods of studying multi-step electrochemical reactions. For example, electrochemical measurements have been used successfully in conjunction with radiochemical measurements[3] to study isotope exchange effects in a multi-step electrode process[40].

More recently the rotating disk electrode with guard ring[41] has been used increasingly in studies of the multi-step anodic dissolution or cathodic deposition of metals, with identification of the unstable intermediate species involved. The multi-step electrode reaction takes place on the central (disk) electrode, and the current i_D is measured as a function of ϕ_D for this electrode. The products of the intermediate steps diffuse from the disk towards the ring, where they react, producing a current i_R. By studying the dependence of i_R on i_D for different speeds of rotation of the disk we can determine the kinetic characteristics of the individual steps in a complex electrode process.

However, in most cases this method also fails to identify the intermediate products directly, and the mechanism of the electrode process has to be inferred from assumed kinetic schemes for the separate reactions. Nevertheless by exploiting recent advances (including progress in computing techniques) we are able to identify the mechanism of the individual steps and the nature of the short-lived intermediate products in a number of electrode processes. For example, evidence has been obtained for the formation of the following lower-valency ions: Al^+ (in the dissolution of aluminium in anhydrous acetic acid[42]), and Be^+ in the dissolution of beryllium[43,44]. An interesting feature of the

dissolution of beryllium is the possibility of a two-electron mechanism (giving Be^{2+}) in parallel with the one-electron mechanism (giving Be^{+}). The lifetime of Be^{+} in solution is $\sim 10^{-2}$–10^{-1} s.

However, the formation of Mg^{+} during anodic dissolution of magnesium in Na_2SO_4 and NaBr solutions could not be established, suggesting that this species is very rapidly removed by a homogeneous reaction (in times ≤ 0.1 s).[45,46] The formation of Bi^{+} ions during the anodic dissolution of the metal in concentrated perchloric acid has been observed[47], and the criteria for the electrochemical and for the chemical mechanism of formation of Cu^{+} in the reaction between Cu^{0} and Cu^{2+} in 1 *N* H_2SO_4 solution have been determined[48].

Current views on the step mechanisms of electrode processes, with formation of intermediate ions in unusual and unstable states of oxidation, are based on the application of multi-step mechanism criteria to a large number of electrochemical processes, not only on amalgam electrodes but also in the dissolution and deposition of multivalent metals on solid electrodes. A detailed discussion of the many publications on this topic lies beyond the scope of the present review, and is largely covered by previous reviews[1,49–52].

The results outlined above suggest that the role of multi-step reactions in electrochemical processes is an important, and even a dominant one. Hence the direct experimental observation of metal ions in intermediate valency states in aqueous or other solutions, even if prepared by non-electrochemical methods, and the study of the nature and properties of these ions may be of great value in the development and validation of our views on the mechanism of step reactions.

III. METAL IONS IN UNUSUAL AND UNSTABLE STATES OF OXIDATION

Recent developments in the pulse radiolysis method and in the matrix stabilisation of short-lived ions and radicals by low-temperature radiolysis have led to the preparation of many metal ions (in aqueous solutions) in unusual and unstable states of oxidation, and to studies of the properties of these ions.

1. Radiation-chemical Preparation

The hydrated electron e^{-}_{aq} and the hydroxyl radical OH, which are formed during the radiolysis of water and of aqueous solutions, have well defined reducing [$E^{0}(e^{-}_{aq}/\frac{1}{2}H_2) = -2.9$ V] and oxidising properties [$E^{0}(OH/H_2O) = 2.8$ V] respectively. Hence the irradiation of many salt solutions can yield, as a result of fast one-electron reduction of metal ions by hydrated electrons

$$M^{n+}_{aq} + e^{-}_{aq} \rightarrow M^{(n-1)+}_{aq} \qquad (10)$$

or fast one-electron oxidation by OH radicals

$$M^{n+}_{aq} + OH \rightarrow M^{(n+1)+}_{aq} , \qquad (11)$$

short-lived metal ions in intermediate states of oxidation which are chemically very active.

The nature and properties of these ions in liquid solutions have been studied by pulse radiolysis with fast recording of the optical spectra and of the changes in electrical conductivity of the medium associated with the formation of these ions[53–58]†. During low-temperature radiolysis of frozen (usually, at 77 K) aqueous salt solutions the metal ions produced by reactions (10) and (11) are stable and can be studied by conventional electron paramagnetic resonance (EPR) and optical spectroscopy methods[57]. The experimental conditions can be chosen so as to favour oxidation or reduction reactions almost totally: this is achieved by adding to the aqueous solution acceptors of e^{-}_{aq} or OH respectively, whose effect is to "transform" the reducing (e^{-}_{aq}) or the oxidising agent (OH) into an oxidising or a reducing agent respectively.

Thus, saturating the solution with N_2O produces the reaction

$$N_2O + e^{-}_{aq} \xrightarrow{H_2O} N_2 + OH + OH^{-} , \qquad (12)$$

as a result of which e^{-}_{aq} is transformed into the OH radical. If the solution is saturated with molecular hydrogen at high pressure the OH radicals give a fairly high yield of active reducing species (hydrogen atoms) by the reaction

$$H_2 + OH \rightarrow H + H_2O .$$

However, the most commonly used additives are organic compounds (RH) such as alcohols, formate ions, etc. which react with OH to give organic radicals R:

$$RH + OH \rightarrow R + H_2O . \qquad (13)$$

The reducing power of these radicals increases in the sequence

$$CH_2OH < CH_3\dot{C}HOH < (CH_3)_2\dot{C}OH < CO^{-}_2 .$$

Even the earliest experiments (in 1963–1965) by the pulse radiolysis method[59–67] demonstrated that e^{-}_{aq} is an active reducing agent towards many metal ions (Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, etc.) in deaerated neutral aqueous solutions of their salts. Later work was concerned with detailed studies of the mechanism of these reactions, and of the nature and properties of the species produced in aqueous solutions of Zn^{2+},[68–70] Cd^{2+},[68,69,71,72] Hg^{2+} and mercury compounds[73–82], Ga^{3+},[83,84] In^{3+},[83] Tl^{+} and Tl^{3+},[85–89] Pb^{2+},[90,91] Bi^{3+},[92] Mn^{2+},[93] Ni^{2+},[68,69,94] Co^{2+},[68,69] Cu^{2+},[95,96] Ag^{+},[97–99] Au^{3+},[100,101] and compounds of Pt[102–105] and Pd.[106]

As well as to these elements, the pulse radiolysis method has been applied to some lanthanides and actinides in unstable states of oxidation, and to a number of complexes (see review in Refs. 53 and 54). It was shown that most of the reactions of e^{-}_{aq} with aquo and chloro complexes of metals are diffusion controlled (10^{9}–10^{10} litre mole^{-1} s^{-1}). The reactivity decreases if water molecules in the coordination sphere of the metal ion are replaced by ligands such as OH^{-}, NH_3, ethylenediamine, glycine, etc. An interesting effect is observed: the rate constant of the reaction between e^{-}_{aq} and M^{n+} falls off most sharply when the last water molecule is replaced by a ligand[67]. Evidently, this arises because the water molecule acts as an electron carrier (from e^{-}_{aq} to the metal ion), being part of the hydration spheres of both species simultaneously. Thus the effect of many ligands (other than water) is to isolate the metal ion from reduction by the e^{-}_{aq} species.

2. Optical Properties

Metal ions in unstable states of oxidation usually absorb in the u.v. region of the optical spectrum with high extinction coefficients (Table 1). The absorption spectrum of metal aquo complexes with an electronic configuration of the outer shells of the $(N-1)d^{10}Ns^{1}$ type, where N is the number of the period (Ag^{0}, Zn^{+}, Ga^{2+}, etc.), consists of a single bell-shaped band. For ions having iso-electronic structures,

†The principles used in pulse radiolysis and various experimental approaches to the determination of the physicochemical parameters of short-lived particles are examined in detail in a special monograph[54].

i.e. for ions of elements in the same period, the absorption band is shifted towards the short-wavelength u.v. region as the charge on the aquo complex increases. An almost linear dependence of the optical transition energy ($E_{\lambda_{max}}$) on the ionic charge is observed[107,108].

Table 1. Optical absorption of metals in unstable states of oxidation in aqueous solutions (λ, nm; ε, litre mole^{-1} cm^{-1}).

Particle	pH	λ_{max}	$10^{-3}\varepsilon$	References
Ag^0	5—7	360	—	[66, 97]
Zn^+	5—7	300	7.5	[68]
Zn^+	5—7	300	13	[70]
Cd^+	3—7	300	13	[68]
Hg^+	2—4.3	255	14	[74]
HgOH	5.5—7.0	233; 265 sh.	10; 5 sh.	[76]
HgCl	1—7	245; 330 sh.	7.5; 2.3 sh.	[75]
HgBr	1—7	280; 350 sh.	5.1; 4.3 sh.	[78]
HgI	1—7	360	5.5	[79]
HgCN	1—7	285	(3.5—3.8)	[77, 81]
HgCNS	1—7	415	4.4	[81]
$Hg_2(I)$	1—3.5	285; 300 sh.	14; 9	[82]
Ga^{2+}	$\leqslant$2.3	265	6.4	[83, 84]
GaOH$^+$	2.9—3.9	265; 300 sh.	5.7	[84]
In^{2+}	$\leqslant$2.0	$\sim$250	20	[83]
Tl^{2+}	$<$1.0	$\leqslant$225	12	[86]
TlOH$^+$		$\leqslant$250; 360 sh.	3.0	[89]
TlCl$^+$	1 M $HClO_4$	263; 342 sh.	7.7; 4.4 sh.	[87]
$TlCl_2$	1 M $HClO_4$	280; 342 sh.	6.4; 4.7 sh.	[87]
$TlCl_3^-$	1 M $HClO_4$	304; 362 sh.	10; 9.3 sh.	[87]
Pb^+	3—4	300	3.0	[90, 91]
Pb^{3+}	3—4	200		[91]
Bi^{2+}	5—7	335		[92]
Co^+	5—7	320; 375	2.3 (311 nm)	[68]
Ni^+	5—7	300	3.6; 6	[68, 94]
Cu^{3+}	2	265	1.1	[66, 95]
CuOH$^+$	5, 7	295	5.7	[95]
Mn^+	5—7	$\sim$300		[63]
Mn^{3+}	5—7	$<$250	2.1 (258 nm)	[93]
$AuCl_2$	$<$2	270	5	[101]
$AuCl_3^-$	$<$2	260	8	[101]
$AuCl_4^{2-}$	$<$2	330	5	[101]
Pt(III)	1—13, Cl^-	410	$\sim$3.5	[102, 103]
Pt(III)	7, Cl^-	450	2.8	[103]
Pt(I)	1—12, Cl^-	310	$\sim$3	[102, 103]
Pt(I)	12, CN^-	360; 295 sh.	8.4 (360 nm)	[102]
Pd(I)	7, Cl^-	$\sim$340		[106]
Pd(III)	7, Cl^-	320	4.7	[106]
Pd(III)	1 M HCl	340	18	[106]

The absorption of the aquo complexes of metals in the *s* and *p* blocks, i.e. elements in subgroups IB—VB of the Periodic Table, in the $^2S_{1/2}$ electronic state (with an unpaired electron in the *s* orbital), is due to a transition of the $a_{1g}^* \rightarrow t_{1u}^*$ type[108]. This transition can be interpreted qualitatively as the transfer of electron density from the central metal ion towards the ligands. In the case of aquo complexes with an octahedral structure a substantial covalent contribution to the formation of the M—OH_2 chemical bond has been demonstrated by the semi-empirical variant of the MO method. This contribution increases with the charge on the central metal ion.

The chloro complexes of Group IB—VB metals show a large number of absorption bands due to $2t_{1u} \rightarrow a_{1g}^*$ and $3t_{1u} \rightarrow a_{1g}^*$ transitions (for complexes with an octahedral structure), i.e. the electron transfer is from the ligands towards the central atom. In contrast to the aquo complexes, the energy of the optical transition ($E_{\lambda_{max}}$) decreases along an isoelectronic series of metal ions as the formal state of oxidation increases[109].

In the optical spectra of the hydroxo complexes (MOH^{m+}, where $m = [(n-1)\pm1]$) we observe a splitting of the fundamental band, characteristic of the $M^{(n\pm1)+}$ ions (Table 1). The compounds HgX (where X = Cl, Br, I, CN) behave similarly[81].

3. State of the Metal Ions in Aqueous Solutions

Metal ions in aqueous solutions react with water molecules or with the anions present in solution to give complexes whose composition and structure are determined to a large extent by the nature and concentration of the anions and by the pH. Reduction or oxidation of the metal ion alters its electronic configuration, often leading to a change in the coordination number, polarisability, and other related characteristics of the ion. The crystallographic radii of the metal ions of Groups IB—IVB in their higher state of oxidation [$(N-1)d^{10}$ electronic configuration] and in a state of oxidation one unit lower [$(N-1)d^{10}Ns^1$ electronic configuration] are compared in Table 2. In the latter case the radii for the iso-electronic series were calculated[108] by the Pauling formula[110]

$$r_Z = \frac{C_{N-}}{Z^*_{\text{eff}}} Z^{-2/(N_B-1)} ,$$

where Z^*_{eff} is the effective charge on the nucleus, Z is the atomic number of the element, N_B is the Born repulsion coefficient, and C_N is a constant coefficient for the iso-electronic series of ions of the elements of periods 4, 5, and 6, determined from the known radii of Cu^0, Ag^0, and Au^0. Since $r[M^{(n-1)+}] > r(M^{n+})$, we can expect the acid-base properties of metal ions in unusual states of oxidation to be different from those of the same ions in the higher states of oxidation. The tendency of the ions to form complexes with dissolved ligands, and other properties, will also be different. This conclusion is borne out by pulse radiolysis studies.

Table 2. Crystallographic radii of the ions of Group IB—IVB metals[108].

M^{n+}	Cu^+	Zn^{2+}	Ga^{3+}	Ge^{4+}	Ag^+	Cd^{2+}	In^{3+}	Sn^{4+}	Au^+	Hg^{2+}	Tl^{3+}	Pb^{4+}
$r(M^{n+})$	0.96	0.74	0.62	0.53	1.26	0.97	0.81	0.71	1.37	1.10	0.95	0.84
$M^{(n-1)+}$	Cu^0	Zn^+	Ga^{2+}	Ge^{3+}	Ag^0	Cd^+	In^{2+}	Sn^{3+}	Au^0	Hg^+	Tl^{2+}	Pb^{3+}
$r(M^{(n-1)+})$	1.278	1.063	0.908	0.791	1.445	1.224	1.059	0.934	1.442	1.244	1.094	0.975

Table 3. Stability constants of chloro complexes for Tl(I), Tl(II), and Tl(III) in aqueous solutions.

Complex	Medium	K_I	K_{II}	K_{III}	K_{IV}	Refs.
$TlCl_3^{2-}$	4 M $NaClO_4$	0.8	0.2	0.1	—	[111]
$TlCl_3^-$	1 M $HClO_4$	$6.2\cdot10^4$	$1.9\cdot10^3$	13	—	[87]
$TlCl_4^-$	0.5 M $HClO_4$	$5.2\cdot10^6$	$1.3\cdot10^5$	553	44	[112]

Dodson and Schwarz[87] studied the chloro complexes of Tl(II)# and calculated their stability constants:

$$Tl^{2+} + Cl^- \overset{K_I}{\rightleftarrows} TlCl^+ ,$$

$$TlCl^+ + Cl^- \overset{K_{II}}{\rightleftarrows} TlCl_2 ,$$

$$TlCl_2 + Cl^- \overset{K_{III}}{\rightleftarrows} TlCl_3^- .$$

#Throughout this paper we shall use a Roman numeral in brackets to denote the state of oxidation of the element.

The constants are compared in Table 3 with the corresponding values for the stable forms Tl(I) and Tl(III). We note that the stability constant increases very rapidly with the charge on the central thallium ion. The tendency of the metal ions to hydrolyse in aqueous solutions varies in a similar way.

For example, the pK values of the reaction

$$M(H_2O)_6^{n+} \rightleftarrows M(H_2O)_5OH^{(n-1)+} + H^+ \qquad (14)$$

for Hg^{2+}, Ga^{3+}, and Tl^{3+} are 3.5, 2.6, and 1.3 respectively[113], and those for Hg^+, Ga^{2+}, and Tl^{2+} are 5.1,[75] ≥3.3,[84] and 4.6.[88] Thus the tendency of metal ions to replace water molecules in their coordination sphere by OH^- ions is decreased by one-electron reduction of the ions, i.e. the ions become less hydrolysable than ions in the higher state of oxidation. Conversely, Cu^{3+} ions obtained from the oxidation of Cu^{2+} by OH radicals [reaction (11)] are more readily hydrolysed than Cu^{2+} ions. The pK of reaction (14) for Cu^{3+} is ~2.9,[64,95] i.e. it is much lower than the pK value for Cu^{2+} (given[113] as 7.5).

We should stress that the formation (during intermediate steps) of metal ions in unusual and unstable states of oxidation almost invariably makes the kinetics of the overall electrode process a function of pH and of the concentration of anions. This may be due to the large difference between the acid–base properties of metal ions in unusual states of oxidation and those of the same ions in their normal states of oxidation. Evidence for this suggestion was given above in connection with the discharge (ionisation) reactions of In [28,29] and Bi [30] on an amalgam electrode. The adsorption of OH^-, Cl^-, SO_4^{2-}, and other anions on the electrode surface and the formation of complexes with the metals in solution can affect the kinetics of the electrochemical act. It is thought, for example, that the adsorption of OH^- groups on an electrode assists the transfer of Fe,[114–116] Ni,[117] and Co [118] into the solution through the intermediate formation of the hydroxo complexes MOH, i.e. that the OH^- ions favour the dissolution of the metal by a multi-step mechanism (see reviews in Refs. 49–51).

The stability of metal ions in unusual states of oxidation in aqueous solutions is determined by the nature of the ligand and by the extent of complex formation by the ion. Thus, the rate constant of the disproportionation of the Tl^{2+}, $Tl(OH)^+$, and $Tl(OH)_2$ ions increases very markedly with the number of hydroxyl groups in the coordination sphere[89]. A similar effect is produced by Cl^- ions in the chloro complexes of Tl(II) [87] and Au(II).[101] Thus by varying the pH or the concentration of ions in solution we can influence the stability of metal ions in unusual states of oxidation, their steady-state concentration, and therefore also the kinetics of the electrode process.

4. Oxidation–Reduction Potentials

The step mechanism of complex electrochemical processes arises, essentially, from differences in the thermodynamic conditions appropriate to each of the constituent acts: in other words, if the redox potentials of the M^+/M and M^{2+}/M^+ pairs in the overall electrode process

$$M \rightleftarrows M^{2+} + 2e \qquad (15)$$

are significantly different we can expect a difference also in the rates of the ionisation and discharge reactions

$$M \rightleftarrows M^+ + e, \qquad (16)$$

$$M^+ \rightleftarrows M^{2+} + e. \qquad (17)$$

Of course, the probability of transfer of several electrons in the same elementary act is in general smaller than the probability of one-electron transfer. Furthermore, the activation energies for the one-step discharge of the M^{2+} ions may be higher than those for the multi-step process involving the formation of intermediate M^+ species[3]. The rate of the slowest step will determine the rate of the electrode process. We shall assume, as usual, that diffusional limitations are absent, i.e. that the reactants diffuse rapidly and their concentrations at the surface and in the volume of the solution are equal. For the metal ionisation–discharge reaction considered here the rates of steps (16) and (17) in the anodic and the cathodic process are given by Eqns.(6) and (7) respectively.

To determine the redox potential of the reaction

$$Red^- + Ox \underset{k_-}{\overset{k_+}{\rightleftarrows}} Red + Ox^- \qquad (18)$$

we need to know the equilibrium constant $K_p = k_+/k_-$. Since metal ions in unusual states of oxidation are active and short-lived particles, reactions involving these ions are usually irreversible, and it is very seldom possible to determine k_+ and k_- simultaneously. It is more usual to determine the rate constant of the forward reaction (for example, the reduction of the metal ions, or their oxidation by the OH radicals to ions in unstable states of oxidation) and that of the subsequent reaction (disproportionation, or interaction with other species present in solution). In any case, the concentrations of different participants in a fast reaction of the type of (18) are always difficult to measure simultaneously because of the overlap of the optical spectra, which interferes with the determination of K_p.

The equilibrium constant of the reaction

$$Tl^{3+} + Fe^{2+} \rightleftarrows Tl^{2+} + Fe^{3+}$$

was determined[86] as 4.1×10^{-8} in 1 M $HClO_4$ solution, and by combining this value with the potential of the Fe^{3+}/Fe^{2+} couple we obtain a potential of 0.3 V for the Tl^{3+}/Tl^{2+} couple. The reactions of Zn^+ and Cd^+ ions with $Co(NH_3)_6^{3+}$ were studied by Navon and Meyerstein[119]: using the standard rate constants for the $Co^{3+} \rightleftharpoons Co^{2+}$, $Zn^{2+} \rightleftharpoons Zn^+$, and $Cd^{2+} \rightleftharpoons Cd^+$ exchange reactions they determined K_p by the Marcus theory[120,121] and they calculated $E^0(Zn^{2+}/Zn^+) = -(2.0 \pm 0.4)$ V and $E^0(Cd^{2+}/Cd^+) = -(1.8 \pm 0.4)$ V. Systematic determinations of the potentials of metals in unusual oxidation states have been carried out by approximate theoretical methods as well as experimentally.

In order to calculate thermodynamically the redox potential of the $M^{n+}/M^{(n-1)+}$ couple we must evaluate the free energy ΔF of the reaction

$$M^{n+} + \frac{1}{2}H_2 \rightarrow M^{(n-1)+} + H^+. \qquad (19)$$

We therefore have to examine the constituent steps of the reaction, whose free energies are usually known [except that for the hydration of the $M^{(n-1)+}$ ion]. It has been assumed[122] that in a reaction such as (19), in which M^{n+} is a bivalent cation, the dependence of $\Delta G_{hydr}(M^+)$ on the ionic radius is the same as for the alkali metals. Furthermore, the M^+ radii were not known, and they had to be found by an approximate method. Thus, the radius of the Zn^+ ion was taken to be the mean of the Cu^+ and Zn^{2+} radii. In this way the $E^0(Zn^{2+}/Zn^+)$ potential was obtained from two values corresponding to the redox potentials of alkali metals having radii equal to those of Zn^{2+} and Cu^+. Similarly, for Cd^+, Pb^+, Mg^+, Ca^+, and Ba^+ the lower values of r_i were identified with those of the Cd^{2+}, Pb^{2+}, Mg^{2+}, Ca^{2+}, and Ba^{2+} ions, and the upper values with those of Ag^+, Tl^+, Na^+, K^+, and Cs^+ respectively. In the

case of Mn^+, Fe^+, Co^+, and Ni^+ the radii were assumed to be the same as for the same metals in the bivalent state.

Values of $E^0[M^{n+}/M^{(n-1)+}]$ obtained in this way are listed in Table 4. Obviously, these values are tentative, but nevertheless in many cases they agree well with experiment. For example, e^-_{aq} does reduce Zn^{2+}, Cd^{2+}, and Pb^{2+} but not Mg^{2+}, Ca^{2+}, or Ba^{2+}. On the other hand the E^0 values obtained for Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} are inconsistent with the observed, fast reactions of these ions with e^-_{aq}. Therefore this method is less attractive, on the whole, than the determination of the potentials by an approximate experimental method, consisting in studying the reactions with R radicals whose potentials (E) are known:

R	e^-_{aq}	H^-	CO_2^-	$(CH_3)_2COH$	CH_3CHOH	CH_2OH	OH	HO_2
E, V	−2.9	−2.3	−2.0	−1.8	−1.1	−0.97	2.8	1.7

Table 4. Redox potentials of metal ions in unstable states of oxidation.

M^{n+}	Calculation (Ref.122)			Experiment
	$r_{(M^{(n-1)+})}$, Å	Hydration energy of $M^{(n-1)+}$, kcal g-ion^{-1}	$E^0(M^{n+}/M^{(n-1)+})$, V	$E^0(M^{n+}/M^{(n-1)+})$, V
Zn^{2+}	0.74—0.96	112—98	−(2.5—3.2)	−(2.4±0.2) [70] *; −(2.0±0.4) [119]
Cd^{2+}	0.97—1.26	98—84	−(1.9—2.5)	−(1.9±0.1) [72]; −(1.8±0.4) [119]
Hg^{2+}	—	—	—	−(1.4±0.3) **
Ga^{3+}	—	—	—	~ −0.65 [123]
In^{3+}	—	—	—	~ −0.45 [123]
Tl^{3+}	—	—	—	+0.3 [86]
Sn^{4+}	—	—	—	+0.7 [124]
Pb^{2+}	1.20—1.40	78—69	−(1.1—1.5)	−(1.0±0.1) [90]
Pb^{4+}	—	—	—	+(1.8±0.3) **
Mn^{2+}	0.8	108	−3.1	~ −2.0 [63, 93] *
Fe^{2+}	0.76	110	−3.1	−(2.7)±2.3) [63, 125] *
Co^{2+}	0.74	112	−3.1	⩾−2.7 [63, 68, 69] *
Ni^{2+}	0.72	113	−2.7	−2.7 [94]
Mg^{2+}	0.65—0.95	118—98	−(4.0—4.8)	<−2.7 [53, 67] *
Ca^{2+}	0.99—1.33	97—81	−(4.8—5.5)	<−2.7 [53, 67] *
Ba^{2+}	1.35—1.69	80—68	−(4.6—5.1)	<−2.7 [53, 67] *

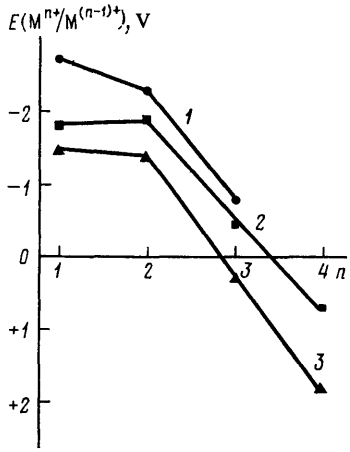
*Obtained from published data on the reactions of M^{n+} with e^-_{aq}, H, and organic radicals.

**Obtained from the dependence of E^0 on the ionic charge in a period and in a group (see Figure).

A study by pulse radiolysis of aqueous solutions of Zn^{2+} has shown[70] that e^-_{aq} reacts with Zn^{2+} to give Zn^+. On the other hand, H atoms reduce Zn^{2+} either very slowly or not at all. Hence we may assume that $E^0(Zn^{2+}/Zn^+)$ is smaller than −2.9 V in absolute value, and close to −2.3 V. There is some justification for assuming a value of −(2.4 ± 0.2 V), which is consistent with that calculated by Navon[119] [−(2.0 ± 0.4) V].

The Cd^{2+} ion is reduced by H and by the CO_2^- radical as well as by e^-_{aq}, but not by alcohol radicals, which have been shown to oxidise Cd^{2+}. It was concluded[72] that $E^0(Cd^{2+}/Cd^+) \cong$ 1.9 V. Potentials determined by this method for metals in aqueous solutions are listed in Table 4.

The variation of these potentials with the charge on the ion is shown in the Figure for the iso-electronic series of ions of metals in periods 4, 5, and 6. The first members of these series are copper, silver, and gold respectively. The redox potentials usually quoted for these metals[123] apply to reactions on a metallic electrode. In the case of metal atoms produced in the volume of the solution the potential must be corrected for the free energy of sublimation at room temperature ΔG^0_{sub}. By subtracting $\Delta G^0_{sub}/e$ (where e is the charge) from $E^0(M^+/M_{sol})$ we obtain the following values of $E^0(M^+/M_{at})$ for copper, silver, and gold respectively: −2.7, −1.8, and −1.5 V.



Redox potential of the $M^{n+}/M^{(n-1)+}$ couple against charge n for ions of metals in the 4th period (Cu, Zn, Ga, curve *1*), the 5th period (Ag, Cd, In, Sn, curve *2*), and the 6th period (Au, Hg, Tl, Pb, curve *3*); see also text.

We note from the Figure that within each subgroup (i.e. for equally charged ions) the quantity $E^0[M^{n+}/M^{(n-1)+}]$ increases regularly with the period number. Furthermore, within any one period (i.e. for iso-electronic ions) the $E^0[M^{n+}/M^{(n-1)+}]$ value increases strongly with the charge on the cation. For example, the metal ions in the electronic $^2S_{1/2}$ state with an unpaired electron in the s orbital which occur in the second subgroup (Zn^+, Cd^+, and Hg^+) are strong reducing agents, whereas those in the fourth subgroup (Sn^{3+} and Pb^{3+}) act as effective oxidising agents.

Having established the dependence of E^0 on the position of the element in its period and subgroup we are able to predict values of the potential. Thus $E^0(Hg^{2+}/Hg^+)$ should be −(1.4 ± 0.3) V, and $E^0(Pb^{4+}/Pb^{3+})$ should be +(1.8 ± 0.3) V. Since $E^0(Pb^{4+}/Pb^{2+}) = 1.7$ V,[123] we can calculate the potential $E^0(Pb^{3+}/Pb^{2+})$: +(1.6 ± 0.3) V. This value is consistent with the earlier conclusion that the potential must lie between 1.5 and 2.6 V, since at pH ~4 the Pb^{2+} ions are oxidised by OH radicals but they are oxidised extremely slowly (if at all) by HO_2 radicals[91].

Thus the postulated formation of metal ions in unusual and unstable states of oxidation (Zn^+, In^{2+}, Cd^+, Ga^{2+}, Sn^+, Tl^{2+}, Pb^{3+}, and many others) during the intermediate steps of electrochemical processes is confirmed by radiation-chemical experiments.

IV. REACTIONS OF METAL IONS IN UNUSUAL AND UNSTABLE STATES OF OXIDATION

Special features of the chemical reactions of metal ions in intermediate states of oxidation with each other or with other species present in solution may determine the kinetics

of the electrode process. Reactions of this type taking place in the volume of the solution have been studied by pulse radiolysis in recent years.

1. Disproportionation and Dimerisation Reactions

As for any other chemical reaction, the condition for the spontaneous occurrence of a disproportionation reaction is a gain in energy, i.e. ΔG must be negative. We shall consider two variants of the change in redox potential accompanying an increase in the degree of oxidation of the metal. In the first variant successive increases in the degree of oxidation require increasingly large amounts of energy, i.e. the removal of each electron requires a greater expenditure of energy than that of the previous electron. Under these conditions the redox potential increases monotonically. It is easy to see that in this case the disproportionation reaction

$$2M^{(n-1)+} \rightarrow M^{n+} + M^{(n-2)+} \qquad (20)$$

is impossible: the transition of $M^{(n-1)+}$ to the more highly oxidised state M^{n+} is impossible because it is less exothermic than the transition $M^{(n-1)+} \rightarrow M^{(n-2)+}$ is endothermic. In the second variant the transition $M^{n+} \rightarrow M^{(n-1)+}$ requires a greater expenditure of energy than the transition $M^{(n-1)+} \rightarrow M^{(n-2)+}$, i.e. $E^0[M^{n+}/M^{(n-1)+}] > E^0[M^{(n-1)+}/M^{(n-2)+}]$. In this case the disproportionation reaction is possible, since it leads to a gain of energy in the system ($\Delta G < 0$).

Table 5. Rate constants (litre mole^{-1} s^{-1}) of the recombination of metal ions in unstable states in aqueous solutions.

Reaction	pH	$2k \cdot 10^{9}2k$	References
$2Zn^{+} \rightarrow Zn^{0} + Zn^{2+}$	5—7	0.3	[70]
$2Cd^{+} \rightarrow Cd_2^{2+}$	5—7	3.0	[72]
$2Hg(I) \rightarrow Hg_2^{2+}$	1.9	8.0	[73]
ditto	2.0	4.5	[74]
»	4.3	5.2	[74]
»	2.4	4.2	[80]
»	4.8	3.5	[80]
»	9.8	8.6	[80]
»	10.2—10.8	11.5	[80]
$2HgOH \rightarrow Hg_2(OH)_2$	5—7	4.4	[76]
$2HgCl \rightarrow Hg_2Cl_2$	~7	8.0	[75]
$2HgBr \rightarrow Hg_2Br_2$	5—7	8.0	[78]
$2HgI \rightarrow Hg_2I_2$	5—7	5.0	[79]
$2HgCNS \rightarrow Hg_2(CNS)_2$	~7	6.0	[82]
$2HgCN \rightarrow Hg_2(CN)_2$	5—7	12	[77]
$2Ga(II) \rightarrow Ga(I) + Ga(III)$	2.4—3.0	8.1	[83,84]
$2In(II) \rightarrow In(I) + In(III)$	2.0—2.4	18	[83]
$2Tl^{2+} \rightarrow Tl^{+} + Tl^{3+}$	1 *M* $HClO_4$	0.12	[85]
ditto	»	0.19	[86]
$2TlOH^{+} \rightarrow Tl(I) + Tl(III)$	>5	5.0	[88]
ditto	»	3.7	[89]
$2Tl(OH)_2 \rightarrow Tl(I) + Tl(III)$	>8	6.3	[89]
$2Pb^{+} \rightarrow Pb^{0} + Pb^{2+}$	~5	0.17	[90]
$2PbH^{+} \rightarrow H_2 + Pb^{2+} + Pb$	~5	0.4	[90]
$Ag^{0} + Ag^{+} \rightarrow Ag_2^{+}$	5—7	k=5.9	[97]
$2Ag^{2+} \rightarrow Ag^{+} + Ag^{3+}$	5—7	3.8	[97]
$Tl^{0} + Tl^{+} \rightarrow Tl_2^{+}$	1 *M* $HClO_4$	k>100	[85]
$2Au^{0} \rightarrow Au_2$	1—2	5.0	[100]
$2AuCl_2 \rightarrow Au(I) + Au(III)$	1—2	1.4	[101]
$2Au(Cl_3)^{-} \rightarrow Au(I) + Au(III)$	1—2	0.86	[101]
$2Au(Cl_4)^{2-} \rightarrow Au(I) + Au(III)$	1—2	0.025	[101]
$2Pt(I) \rightarrow Pt^{0} + Pt(II)$	5—7	4.1	[102]
ditto	1—2	2.5	[102]
$2PtCl_4^{-} + Cl^{-} \rightarrow PtCl_4^{2-} + PtCl_6^{2-}$	~2	~1	[103]

Thus the condition for the disproportionation reaction is inversion of the potential energy levels of the system. By comparing the data in Table 4 with the potentials of the same metals in stable valence forms[123] we find level inversion for most of the metals in intermediate states of oxidation, i.e. we find conditions favourable to the fast disappearance of these ions by disproportionation reactions. Studies by the pulse radiolysis method of the disappearance of metal ions in unusual states of oxidation have shown that in most cases recombination is accompanied by disproportionation (Table 5).

An obvious exception to this rule are the metal ions having one unpaired electron in an *s* or *p* orbital and a low charge (0 or 1), such as Ag^0, Cd^+, and Hg^+ (whose electronic shell has the $(N-1)d^{10}Ns^1$ configuration), or Tl^0 and Pb^+ [$(N-1)d^{10}Ns^2Np^1$ shell]. These particles tend to form dimers in which the unpaired electrons are shared in σ_s or σ_{p_z} bonds. Thus, Cd^+ and Hg^+ ions undergo fast recombination, forming Cd_2^{2+} and Hg_2^{2+} ions. More surprisingly, Cd^+, Hg^+, and other ions of this type can also form unstable dimeric particles of the type of Cd_2^{3+}, Hg_2^{3+}, etc. in which the two atoms are joined by a one-electron bond (half a covalent bond). Thus it has been shown that Ag^0 atoms[97-99] and Tl^0 atoms[85-89] formed by the reduction of Hg^+ and Tl^+ ions (at concentration $>10^{-5}$ M) by hydrated electrons disappear by the pseudo-first order reaction

$$Ag^0 + Ag^+ \rightarrow Ag_2^+ ,$$
$$Tl^0 + Tl^+ \rightarrow Tl_2^+ .$$

Direct evidence of the existence of the Ag_2^+ ion has been obtained[126-128] by ESR during the low-temperature (77 K) radiolysis of aqueous solutions of Ag^+. The effect of the initial concentration of Cd^{2+} ions on the disappearance of Cd^+ ions in aqueous solutions containing methanol has been studied[69] by pulse radiolysis. In 0.1 M solutions of Cd^{2+} the Cd^+ ions disappear by a pseudo-first order reaction, and a relatively long-lived absorption at 280 nm is observed after the absorption corresponding to Cd^+ ions has completely disappeared. No suggestion has been put forward[69] as to the nature of this absorption. One possibility is the reaction of Cd^+ with Cd^{2+} ions:

$$Cd^+ + Cd^{2+} \rightarrow Cd_2^{3+} . \qquad (21)$$

The formation of paramagnetic dimeric Cd_2^{3+} ions has been detected by ESR and optical spectroscopy methods in glassy aqueous solutions containing 0.1 M $CdSO_4$ gamma-irradiated at 77 K.[129,130]. The maximum optical absorption of Cd_2^{3+} in the solid matrix also occurs at ~280 nm. This ion is stabilised, apparently, by the collectivisation of one unpaired electron on the Cd—Cd σ bond. The rate constant of reaction (21) is much lower than that of the recombination of Cd^+ ions, and therefore reaction (21) is predominant only at high concentrations of Cd^{2+} ions. The existence of Hg_2^{3+} particles also has been established by ESR and optical spectroscopy methods in the low-temperature gamma-radiolysis of aqueous solutions of Ag^{2+}.[129,130].

Pb^+ ions are structurally iso-electronic with Tl^0, and therefore we can expect them to decay by the following reaction at high concentrations of Pb^{2+} ions in solution:

$$Pb^+ + Pb^{2+} \rightarrow Pb_2^{3+} .$$

There are no data on this reaction for liquid aqueous solutions, but the formation of Pb_2^{3+} particles during the low-temperature gamma-radiolysis of acidic or alkaline solutions of Pb^{2+} has been observed by optical spectroscopy[131,132].

For the Ga^{2+}, In^{2+}, Tl^+ and other ions the formation of dimers by recombination is not typical, possibly owing to the predominance of electrostatic repulsion. We have shown[83,84] that the loss of Ga^{2+} and In^{2+} is by a second-order reaction, involving disproportionation or interaction with OH radicals. The reactions of Tl(II) have been studied by pulse radiolysis of deaerated aqueous solutions containing Tl(I) and Tl(III).[85-89] Under these conditions the reactions between

e^-_{aq} and Tl(III), and between OH and Tl(I), yield only Tl(II). The latter have been shown to disappear by the reaction

$$Tl(II) + Tl(II) \rightarrow Tl(I) + Tl(III)$$

whose rate constant is strongly influenced by the presence of Cl^- ions in the solution[87], and also by the pH.[88,89] Pb^+ ions disproportionate with formation of Pb^0, which gives an absorption with $\lambda_{max} < 250$ nm.[90]

In the absence of acceptors of OH radicals the disappearance of transition metal ions in unstable states of oxidation (Mn^+, Co^+, Ni^+, etc.) is by a second-order reaction[62-67,93,94], evidently through interaction of the ions with each other and with the OH radicals. In the presence of organic compounds (acceptors of OH radicals) the univalent ions disappear by more complex reactions with formation of metal–organic intermediates.

2. Reactions with Inorganic Compounds

The effect of various additives on the kinetics of electrode processes, and in particular on metal corrosion, may be related to the reactions of these additives with metal ions in unstable states. The mechanism of the reactions of Zn^+, Cd^+, and Ni^+, and of many other metal ions, with various inorganic compounds (O_2, H_2O_2, N_2O, NO_2^-, NO_3^-, BrO_3^-, IO_3^-, etc.) has been studied by the pulse radiolysis method[65,69,70,133-138]. The metal ions have been shown to reduce these compounds at fairly high rates. The rate constants of the reactions of Zn^+, Cd^+, Ni^+, and Co^+ ions with some inorganic compounds in aqueous solutions are compared in Table 6 with the corresponding rate constants for the strongly reducing agents e^-_{aq} and H.

The ions can be arranged in the following series in order of decreasing reactivity towards inorganic oxidising ions: $Zn^+ \geq Cd^+ > Co^+ > Pb^+ > Ni^+ > Hg^+ \geq Cr^{2+} > Cu^+$. However, there are many exceptions: for example, with molecular O_2 the Ni^+ ion reacts almost as fast as Zn^+ and Cd^+, and Co^+ reacts even faster. The reactivity is determined by the electronic structure of the ions, by the nature of the acceptor, and by the specific mechanism of the oxidation–reduction reaction. In the Zn^+ and Cd^+ ions the electron is localised on the outer *s* orbital, with a substantial shift into the outer sphere. As a result, these ions are strong reducing agents. However, even between Zn^+ and Cd^+ we observe a decrease in reactivity towards several oxidising agents (see Table 6).

This decrease is even more marked in Hg^+. Thus the rate constant of the reaction between Hg^+ and O_2 was found[80] to be 4×10^8 litre mole^{-1} s^{-1}, i.e. almost an order of magnitude smaller than the values for Zn^+ and Cd^+. This decrease in reactivity in the Zn–Cd–Hg group is easily explained by noting that the stability of the lower states of oxidation for this group of metals increases in the same sequence, and that the Hg^+ ion is a fairly stable species (for example, in the dimeric form). In the transition metals an additional electron is accommodated in an inner *d* orbital, and as a result the ions are less active as reducing agents than the Zn^+ or Cd^+ ions.

We should stress that the reactivity sequence of the $M^{(n-1)+}$ ions is not the inverse of the reactivity sequence of M^{n+} towards e^-_{aq}. No definite correlation has been noted between the relative rate constants for the reactions of e^-_{aq}, H, and the $M^{(n-1)+}$ ions, suggesting that different mechanisms may apply to the redox reactions of these particles. For example, $M^{(n-1)+}$ (unlike e^-_{aq}) reacts very slowly with H_3O^+, or not at all. A possible explanation is that the redox potential of the $M^{(n-1)+}$ ions is too low, in general, to allow these ions to reduce H_3O^+.

Because of their technological importance we shall examine in somewhat greater detail the reactions between the lower-valency forms of metals and molecular oxygen in corrosion processes, and we shall discuss their mechanism. The reactions of Ag^0, Hg^0, Zn^+, Cd^+, Pb^+, Cu^+, Co^+, Ni^+, and Cr^{2+} with molecular O_2 have been studied by pulse radiolysis, and their rate constants have been measured (Table 7). With the exception of Cu^+, Ni^+, and Cr^{2+} these ions were found to be oxidised with formation of the O_2^- ion radical:

$$M^{(n-1)+} + O_2 \rightarrow M^{n+} + O_2^- \quad . \qquad (22)$$

Table 7. Rate constants for the oxidation of metals in unstable states by O_2 in aqueous solutions (litre mole^{-1} s^{-1}).

Species*	$10^{-8}\,k$	Species	$10^{-8}\,k$
Ag_2^+	3.8 [133]	Hg_2 (I)	11 [82]
Au^0	36 [100]	HgCl	10 [75]
Cd^+	30 [138]	Ni^+	18 [65,133]
Co^+	60 [138]	Pb^+	39 [65]
Cr^{2+}	1.6 [137]	$Pt(CN)_4^{3-}$	0.18 [102]
Hg^+	4.0 [80]	Zn^+	28 [65,133]

*For Cu^+ we have $k \leq 10^{-6}$ litre mole^{-1} s^{-1}.[133]

Table 6. Rate constants of the reactions of e^-_{aq}, H, and $M^{(n-1)+}_{aq}$ with inorganic compounds in aqueous solutions (litre mole^{-1} s^{-1}).

Compound	e^-_{aq}*	H*	Zn+	Cd+	Ni+	Co+
N_2O	$5.6 \cdot 10^9$	$1.2 \cdot 10^4$	$1.3 \cdot 10^7$ [133]	$2 \cdot 10^6$ [133]	$6.3 \cdot 10^6$ [133]	$1.0 \cdot 10^9$ [138]
	—	—	$3.7 \cdot 10^6$ [138]	$3.5 \cdot 10^6$ [138]	$9.1 \cdot 10^6$ [138]	—
H_2O_2	$1.23 \cdot 10^9$	$1.6 \cdot 10^8$	$1.8 \cdot 10^8$ [133]	$1.55 \cdot 10^9$ [133]	$4.3 \cdot 10^7$ [133]	$1.6 \cdot 10^9$ [138]
	—	—	$2.3 \cdot 10^9$ [138]	$2.2 \cdot 10^9$ [138]	$3.2 \cdot 10^7$ [138]	—
NO_2^-	$4.6 \cdot 10^9$	$6 \cdot 10^8$	$2.2 \cdot 10^8$ [133]	$2.0 \cdot 10^9$ [133]	$1.5 \cdot 10^8$ [133]	—
NO_3^-	$1.1 \cdot 10^{10}$	$1.7 \cdot 10^7$	$2.1 \cdot 10^9$ [133]	$3.5 \cdot 10^8$ [111]	$1.4 \cdot 10^6$ [133]	$1.8 \cdot 10^8$ [138]
ClO_3^-	$4 \cdot 10^8$	—	$\leqslant 3 \cdot 10^6$ [133]	—	—	—
BrO_3^-	$2.1 \cdot 10^9$	$1.95 \cdot 10^7$	$2.1 \cdot 10^9$ [133]	$1.25 \cdot 10^8$ [133]	$8.4 \cdot 10^6$ [133]	$7.1 \cdot 10^8$ [138]
IO_3^-	$7.7 \cdot 10^9$	$5.9 \cdot 10^7$	$3.6 \cdot 10^9$ [133]	$2.3 \cdot 10^9$ [133]	$2.2 \cdot 10^8$ [133]	$4.3 \cdot 10^8$ [138]
$S_2O_8^{2-}$	$1.1 \cdot 10^{10}$	$2.4 \cdot 10^7$	$1.3 \cdot 10^9$ [138]	$2.4 \cdot 10^9$ [138]	$1.5 \cdot 10^8$ [138]	$2.8 \cdot 10^8$ [138]
CrO_4^{2-}	$1.8 \cdot 10^{10}$	$1.6 \cdot 10^{10}$	$1.6 \cdot 10^{10}$ [138]	$1.6 \cdot 10^{10}$ [138]	—	—
MnO_4^-	$2.6 \cdot 10^{10}$	$2.8 \cdot 10^{10}$	—	$1.3 \cdot 10^{10}$ [65]	$7.5 \cdot 10^9$ [65]	$1.06 \cdot 10^{10}$ [65]
Cu^{2+}	$3.3 \cdot 10^{10}$	$6 \cdot 10^8$	$2.5 \cdot 10^8$ [133]	$1.2 \cdot 10^8$ [133]	$2.4 \cdot 10^7$ [133]	$4.1 \cdot 10^8$ [133]

*Rate constants given in Ref. 53.

For Ni^+ and Cr^{2+} the relatively stable complexes NiO_2^+ and CrO_2^{2+} were identified. The NiO_2^+ complex can be protonated (pK_a = 3.2), and both forms disappear by an intramolecular dissociation reaction giving Ni^{2+} and O_2^- or HO_2.[137-140] The interaction of Cu^+ with O_2 was found[137] to be either very slow or reversible (with a forward reaction much slower than the reverse reaction). The tabulated results show that the formation of stable complexes such as $MO_2^{(n-1)+}$ is characteristic of the transition metals with an unfilled inner *d* orbital. Complex formation involves the transfer of the unshared electron pair of the O_2 molecule to these levels.

The reaction of metals in unstable states of oxidation with H_2O_2 produces OH radicals[133,138]:

$$M^{(n-1)+} + H_2O_2 \rightarrow M^{n+} + OH + OH^- . \quad (23)$$

From the standpoint of corrosion processes reactions (22) and (23) can be interpreted as intermediate steps in the anodic dissolution of the metal. The O_2 and H_2O_2 are often treated as cathodic depolarisers. These species can be actively involved in the intermediate steps, and determine the rate of dissolution of the metal if the reactions take place directly on the anode.

The pulse radiolysis method has been used to prepare and investigate several metal ions in unstable states of oxidation showing strongly oxidising properties. One of these is the Cu(III) ion, which can oxidise the Br^- and NO_2^- ions, alcohols, and H_2O_2.[66,95] It has also been shown[95] that the Cu(III) ion can decompose water with formation of OH radicals by the reversible reaction

$$Cu(III) + H_2O \rightleftarrows Cu(II) + OH + H^+ .$$

The equilibrium constant calculated for this reaction at pH 3.65 (9.0×10^5 mole^{-1} litre) assumes that the redox potential of the Cu^{3+}/Cu^{2+} couple is only 0.2 V lower than the potential of the OH/H_2O couple.

3. Reactions with Organic Compounds

The effect of organic compounds on the kinetics of electrode (metal discharge and ionisation) reactions is usually ascribed to adsorption of these compounds on the electrode, formation of colloidal solutions, etc. Obviously, the participation of organic compounds in the intermediate steps by reaction with metal ions in unusual and unstable states of oxidation cannot be excluded. Reactions of this type have been studied by the pulse radiolysis method far less fully than reactions with inorganic compounds. It has been shown[141] that $M^{(n-1)+}$ is an effective reducing agent (by the one-electron mechanism) for aromatic dyes Ar:

$$M^{(n-1)+} + Ar \rightarrow M^{n+} + Ar^- .$$

The rate constants for the reaction of some ions with *p*-benzoquinone, menaquinone, and benzophenone in aqueous solutions at pH 5–6 are given in Table 8.

The mechanism of the interaction of metals with halogenated aliphatic acids has been shown[142] to include transfer of the halogen atom,

$$M^{(n-1)+} + XCH_2COOH \rightarrow [MXCH_2COOH]^{(n-1)+} ,$$

rather than electron transfer, i.e. the mechanism is the same as for the reaction with the H atom (but not for the reaction with e_{aq}^-).[143]

The Tl^{2+} and Ag^{2+} ions behave as "mild" oxidising agents, and they react with benzoic acid (BA) and methoxybenzoic acid (MBA) with very high rate constants (~10^9 litre mole^{-1} s^{-1}), forming short-lived anion radicals[144,145]:

$$BA(MBA) + Tl^{2+} (or\ Ag^{2+}) \rightarrow BA^{\cdot}(MBA^{\cdot}) + Tl^{+} (or\ Ag^{+}).$$

Derivatives of benzoic acid are widely used as corrosion inhibitors: their effect on the corrosion process may be due at least in part to reactions of this type.

Table 8. Rate constants (10^{-9} *k*, litre mole^{-1} s^{-1}) of the reactions of metal ions with organic compounds in aqueous solutions at pH ~5–6.[141]

Compounds	Cd+	Co+	Ni+	Pb+	Zn+
Benzoquinone	4.8	5.1	0.23	4.1	4.8
Menaquinone	4.6	4.0	2.4	3.7	3.8
Benzophenone	1.0	2.5	—	—	2.5

Note. For the reaction of 2-methoxybenzoic acid (pH ~3) with Ag^{2+} and Tl^{2+} the *k* values are 1.2×10^9 and 6.8×10^8 litre mole^{-1} s^{-1} respectively[144,145].

4. Formation of Intermediate Complexes

Metal ions tend to form unstable complexes in one-electron redox reactions with radicals (H, OH, alcohol radicals, etc.) or with molecular compounds. For example, in the fast oxidation of Fe^{2+} by OH radicals the $FeOH^{2+}$ ion is formed[146]. The reaction of Fe^{2+} with HO_2 radicals, and the reaction of Fe^{3+} with H_2O_2, yield the $Fe^{3+}...HO_2^-$ complex[125], which is unstable and dissociates by a first-order reaction whose rate constant is independent of the pH (in the range pH 0–2.1) and of the concentration of O_2 and Fe^{3+}, but increases slightly with the concentration of Fe^{2+}. The latter effect shows that the decomposition of the complex is catalysed by Fe^{2+} ions, whose participation in the intermediate step of the reaction yields the bridging compounds

$$[Fe^{3+} \ldots HO_2^-] + Fe^{2+} \rightarrow [Fe^{3+} \ldots HO_2^- \ldots Fe^{2+}] \rightarrow Fe^{2+} + Fe^{3+} + HO_2^- .$$

Other transition metal ions (M^{n+}) in aqueous solution react with O_2^- ion radicals to give $MO_2^{(n-1)+}$ complexes. For example, the species MnO_2^+ has been detected[93] by the pulse radiolysis method in aerated aqueous solutions of $Mn(ClO_4)_2$. The equilibrium constant of the reaction

$$MnO_2^+ \rightleftarrows Mn^{2+} + O_2^-$$

was found to be $(1.5 \pm 0.6) \times 10^4$ M^{-1}. As stated above, Ni^+ and Cr^{2+} also interact with molecular oxygen to form the intermediate complexes NiO_2^+ [137,138] and CrO_2^{2+}.[139,140] We must assume that these same complexes are formed by the reaction of Ni^{2+} and Cr^{3+} with the O_2^- ion radical.

Hydrogen atoms react with Fe^{2+} with formation of the unstable hydride FeH^{2+} which disappears by the reaction

$$H^+ + FeH^{2+} \rightarrow Fe^{3+} + H_2$$

with a rate constant of ~1×10^4 litre mole^{-1} s^{-1}.[125] Apparently hydride formation is characteristic also of other transition metals (Co^{2+}, Ni^{2+}, etc.) reacting with H atoms. These metals have an unfilled inner *d* shell. On the other hand, if the metal has a filled inner *d* shell (Hg, Cd, Zn, etc.) these reactions are not observed.

Our results are consistent with the traditional classification of metals into two groups with respect to their electrochemical properties[147,148]. The first group (metals of the platinum group and iron) has a high heat of adsorption of hydrogen atoms, and the rate of evolution of molecular hydrogen from these metals is limited by the chemical

dimerisation reaction of the hydrogen atoms. A likely explanation of these properties is the formation of fairly strong chemical bonds with the metal atoms on the surface of the electrode. The second group of metals (Hg, Cd, Zn, etc.) is characterised by weaker adsorption bonds with hydrogen atoms. The rate-limiting step in the evolution of hydrogen is a slow discharge process. We may assume that the hydrogenation of metals produced by various electrode processes is due to the step mechanism of the discharge (ionisation) reaction, involving the formation of hydride complexes during the intermediate steps.

Metals in unusual states of oxidation react with organic (e.g., alcohol) radicals to form unstable metal–organic compounds[69,72,77,94,149]:

$$M^{(n-1)+} + R \rightarrow MR^{(n-1)+} .$$

These compounds usually show characteristic optical absorption bands in the u.v. region of the spectrum. The life time of the intermediate complexes is determined by the rate of hydrolysis. For example, the cadmium-organic compounds CdR^+ decompose by the reaction

$$CdR^+ + H^+ \rightarrow Cd^{2+} + RH$$

with rate constants 161 s^{-1} for R = $(CH_3)_2COH$ and 257 s^{-1} for R = CH_3CHOH.[72] Nickel–organic compounds are more stable. Their lifetime is ~1 s when R is a methanol or ethanol radical, and even longer for more complex radicals[94]. Nickel compounds are easily oxidised in the presence of H_2O_2. In experiments with aqueous solutions of 2-methyl-2-propanol it was shown[94] that the resulting organic radicals react with Ni^+ to form isobutene:

$$Ni^+ + CH_2C(CH_3)_2OH \rightarrow Ni^{2+} + CH_2{=}C(CH_3)_2 + OH^- .$$

The rate constant of this reaction is 3×10^9 litre $mole^{-1}$ s^{-1}.

The formation of unstable metal–organic compounds has been demonstrated by pulse radiolysis for the reaction of alcohol radicals with Zn^+,[69] HgCN,[77] and the Cr^{2+} ion[149]. Chromium–organic compounds are more stable to hydrolysis than nickel–organic compounds. For example, the compound $CrCH_2OH^{2+}$ decomposes in water with a rate constant of ~7×10^5 s^{-1}.[149]

5. Reduction to Metals

The chemical reduction to a metal from aqueous solutions of its salts must occur through a number of intermediate steps in which the metal displays unusual valency forms. Radiation-chemical methods (and, in particular, the pulse radiolysis method) have proved very useful in studies of the reduction mechanism of the cations and of the nucleation of the metal in aqueous solutions. The chemical steps in the reduction are fairly specific for the individual cations (Ag^+, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Pt^{2+}, etc.) and are usually complex. For example, the Ag^0 atoms produced by a 2 μs pulse of electrons on a 10^{-5} M solution of Ag^+ saturated with argon and containing 0.1 M CH_3OH disappear in a few tens of microseconds by reacting with the Ag^+ ions to form Ag_2^+. The disappearance of the latter is accompanied by the formation of two new particles:

$$Ag_2^+ + Ag^+ \rightarrow Ag^{2+} + Ag_2 .$$

The relatively slow removal of Ag_2 by a pseudo-first order reaction is markedly influenced by the concentration of Ag^+. The reaction is assumed to be

$$Ag_2 + Ag^+ \rightarrow Ag_3^+ .$$

After a few milliseconds we observe a long-lived optical absorption at 390 nm, assigned[97] to the association of Ag_3^+ particles to form agglomerates of metallic silver:

$$Ag_3^+ \rightarrow \text{metal}.$$

These results show that even an apparently simple process such as the nucleation of atomic silver in an aqueous solution of Ag^+ can be complex and involve a number of steps. The reduction of a cation to the metal includes a large number of intermediate steps: one-electron reduction of the cation, disproportionation or dimerisation of the reduction product, cluster formation and growth of the clusters to give massive metal particles. The radiation-chemical reduction of the cations and formation of a metallic deposit is most effective in deaerated, neutral aqueous solutions of the salts containing organic additives such as formate ions, alcohols, etc. The latter act as acceptors of OH radicals, thus preventing back oxidation of the metal ions reduced by solvated electrons or by H atoms.

The formation of metal granules by pulsed irradiation of aqueous salt solutions has been studied in more detail for the cadmium deposition system. It was found[71] that the optical absorption due to the short-lived Cd^+ and Cd_2^{2+} ions (which are the precursors of the metal atoms) disappears ~10^{-4} s after the application of the electron pulse, and the solution becomes fully transparent. The transparent state persists for ~0.1 s, after which a new absorption occurs over the whole of the optical region, increasing to a constant value in ~10 s. The optical density D increases with the fourth power of the wavelength in the u.v. region, a characteristic property of media containing suspended matter which scatters rather than absorbs light.

The effect of the ionic strength of the solution on the rate of formation of finely divided metallic cadmium suggests[72] that the metal is being deposited from complex cadmium clusters having an effective charge of +5.5. The time for nucleation and growth of the metal grains decreases as the supersaturation of the solution increases (i.e. in proportion to the dose of radiation per pulse). A few minutes after the appearance of turbidity in the solution, precipitation of the metal begins, accompanied by a decrease in absorption in the u.v. region of the spectrum and increased absorption at longer wavelengths[72], caused by the increase in size of the metallic agglomerates. The precipitation curves are accurately described by a pseudo-first order equation with respect to Cd^0 concentration, with a rate constant of $(5 \pm 2) \times 10^4$ s^{-1}.[71]

Similar effects have been observed in the formation and deposition of metal by the pulse radiolysis of aqueous solutions of Ag^+ and its ammine complex[97,98], and also of Ni^{2+}.[94] It has been shown[71] that under identical pulsed irradiation conditions the induction period t_0 (time of nucleation) of many salt solutions calculated from the experimentally observed delay in the appearance of turbidity depends on the nature of the cation and decreases in the sequence $Pb^{2+} \cong Cd^{2+} \gg Zn^{2+} > Ni^{2+} > Co^{2+}$.

6. Metal Dissolution

The stability of a metal and its rate of dissolution in aqueous or other solutions is determined by its electrode potential. The rate of dissolution decreases if the potential is shifted towards more negative values, and becomes zero when a definite value of the potential is reached. Alkali and alkaline-earth metals dissolve in water at approximately constant rates. Since their redox potential

is more negative than −2.9 V we can expect hydrated electrons to be formed during their dissolution.

The possibility of forming hydrated electrons by the reaction between sodium amalgam and water has been demonstrated[150,151] by the acceptor competition method:

$$Na\,(Hg) + H_2O \rightarrow Na^+ + e^-_{aq} \quad .$$

This conclusion was based on the detection of N_2 as the main reaction product in an aqueous solution containing N_2O and CH_3OH, by the reaction

$$N_2O + e^-_{aq} \rightarrow N_2 + O^-$$

rather than H_2, expected to be formed by the reaction

$$CH_3OH + H \rightarrow H_2 + CH_2OH$$

if the H atom had been a primary product of the dissolution of sodium amalgam. On the other hand, experiments with pure sodium suggest that several mechanisms contribute to the dissolution of this metal in water (see Ref.53).

It has been suggested[152,153] that the generation of e^-_{aq} can be induced by cathodic polarisation of an electrode. The same conclusion was reached from the observation of a substantial decrease (by ~35%) in the yield of H_2 from a smooth platinum electrode on adding N_2O to a neutral solution. On the other hand the presence of CH_3OH had no effect on the relative yields of N_2 and H_2. These results convincingly demonstrate the participation of an electron in the formation of N_2. However, there is reason to believe that the reaction involving the electron takes place directly on the cathode (with adsorbed N_2O), and not in the bulk of the solution (as it would if the hydrated electron was involved).

The important role of the e^-_{aq} species in the chemical dissolution of metals has been stressed[154], and used as a basis for discussing instability criteria. The first step in the dissolution was assumed to be the formation of an uncharged activated complex,

$$M + H_2O \rightarrow (MH_2O)^* \quad .$$

In the second step this complex dissociates into e^-_{aq} and the metal ion:

$$(MH_2O)^* \rightarrow M^{n+} + ne^-_{aq} \quad .$$

Neither of the steps is electrochemical, since no charge is transferred across the metal–solution interface, and therefore the rate of the overall process should be independent of the potential. However, the rate of dissolution can be expected to depend on the pH, on the nature of the surface, and on the overall current density, and these expectations have been confirmed experimentally.

According to Antropov[154] the condition for self-dissolution of the metal is

$$S_M + \sum_1^n I_{n+} \leqslant A^{H_2O}_{M^{n+}(r)} + nA^{H_2O}_{e^-(r)}$$

where S_M is the free energy of sublimation of the metal, $\sum_1^n I_{n+}$ is the sum of the ionisation potentials (from 1 to n) of the metal, and $A^{H_2O}_{M^{n+}(r)}$ and $A^{H_2O}_{e^-(r)}$ are the real free energies of hydrated M^{n+} ions and electrons respectively. This criterion has been tested for alkali and alkaline-earth metals. However, direct experimental evidence of the formation of e^-_{aq} during cathodic polarisation of the electrode or during chemical dissolution of the metals in water has not yet been obtained.

A detailed critical analysis of these hypotheses is given in Refs.155 and 156. The probability of thermionic emission of an electron into the aqueous solution is believed, on theoretical grounds[157], to be very low, and the contribution from this mechanism to the cathodic currents is probably negligible, even at high negative potentials. On the other hand, the probability of ordinary cathodic reactions (electron transfer to adsorbed ions or molecules) is quite high at these potentials.

Nevertheless the possible formation of e^-_{aq} during the reaction of some metals (such as alkali or alkaline-earth metals) with water cannot be excluded: this is shown, for example, by the reported[158] formation of e^-_{aq} during the condensation of finely divided sodium and potassium with water vapour on a surface cooled to 77 K. We should also note that the cathodic generation of solvated electrons was detected experimentally in solvents which are stable at large negative potentials (hexamethylphosphotriamide, liquid ammonia, some amines, etc.; see review in Ref.159).

Dependence of the rate of corrosion of metals on the nature of the anions suggests that the anions are directly involved in the reaction. According to Kolotyrkin and coworkers[49–51] the anodic dissolution of metals takes place through the formation of a complex the metal (M) and a ligand (L):

$$M + L \rightleftarrows ML \quad .$$

The adsorption of ligands lowers the electronic work function and accelerates the corrosion of the metal:

$$ML \rightarrow ML^{n+} + n\,e^- \quad .$$

The dissolution of iron in acid solutions is now believed[51] to take place through the formation of the unstable intermediate FeOH, in which the iron displays the unusual state of oxidation +1. Evidently, the formation of unstable coordination compounds of the ML^{n+} type during the intermediate stages of the electrochemical or chemical dissolution of metals is a fairly common phenomenon. In the first section of this review we had discussed experimental evidence for the formation of metals in unusual states of oxidation during electrochemical reactions (for example, Zn^+, In^{2+}, Tl^{2+}, etc.). Evidently, in many cases the disproportionation (or dimerisation) of these species is energetically more favourable than further ionisation (see Section IV, Pt.1).

It is important to note that when $E^0[M^{n+}/M^{(n-1)+}] \lesssim E^0(e^-_{aq}/\frac{1}{2}H_2)$ the ionisation of $M^{(n-1)+}$ in aqueous solutions (especially at high pH values) can yield a hydrated electron:

$$M^{(n-1)+}_{aq} \rightarrow M^{n+}_{aq} + e^-_{aq} \quad .$$

The possibility of these reversible reactions has been examined[160] in the case of the interaction of e^-_{aq} with Zn(II) and Al(III) in aqueous solutions of alkalis. More recently it has been shown by the pulse radiolysis method[161,162] that the rate of disappearance of e^-_{aq} decreases (as expected) as the concentration of Zn(II) increases. This effect was explained by postulating the equilibrium reaction

$$e^-_{aq} + Zn\,(OH)_4^{2-} \rightleftarrows Zn\,(OH)_3^{2-} + OH^- \quad . \qquad (24)$$

The equilibrium constant of this reaction for a 3 M solution of LiOH is 0.1 M^{-1}, i.e. the E^0[Zn(II)/Zn(I)] value under these conditions is only ~0.09 V more positive than $E^0(H_2O/e^-_{aq})$.

The redox potentials of the Zn^{2+}/Zn^0 and Al^{3+}/Al^0 couples in acid solution are −0.76 and −1.66 V respectively[123]. In an alkaline medium these metals exist as hydroxo complexes, and the potentials of the $Zn(OH)_4^{2-}/Zn^0$ and $Al(OH)_4^-/Al^0$ couples are more negative (−1.22 and −2.35 V respectively[123]). It follows that the potential of the $Zn(OH)_4^{2-}/Zn(OH)_4^{2-}$ couple also suffers a negative shift [as compared with the potential of the Zn^+/Zn^{2+} couple, ~(−2.4 V)], and thus becomes comparable with $E^0(H_2O/e^-_{aq})$. These considerations allow us to predict reversible reactions of the type of (24) not only for hydroxo complexes of metals in alkaline media but also

for cyano and other complexes in neutral solutions. The latter complexes also experience a large negative shift of the potential[123], and the following condition may apply:

$$E^0(MX_{m-n}^{n-}/MX_{n-n}^{(n+1)-}) \lesssim E^0(e_{aq}^-/{}^1/_2H_2)$$

* *
*

Thus the advances in radiation-chemical (and, in particular, in pulse radiolysis) techniques made in the last 15 years have markedly influenced the new developments in the chemistry of metals in unusual and unstable states of oxidation. The discovery of these short-lived particles, the study of their properties, and the formulation of rules governing those properties will undoubtedly stimulate further developments in the chemistry of the intermediate steps of redox reactions, involving metals in unstable valence forms. Of course, the preparation of various ions in unusual states of oxidation by radiation-chemical methods cannot in any way be taken as evidence for the formation of those same ions during electrochemical reactions. However, the generation of data on the properties of these intermediate particles should greatly assist the study of the mechanism of multi-step electrochemical processes.

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The Reactivity of Hydrogen Atoms

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Theoretical ideas about the reactions of thermal and "hot" hydrogen atoms are examined and experimental data, characterising the mode of reactions involving hydrogen atoms with different energies, are presented.
The bibliography includes 212 references.

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I. INTRODUCTION

The hydrogen atom is the simplest chemical species and has for a long time attracted the attention of investigators endeavouring to understand elementary chemical processes. On the other hand, the role of hydrogen atoms in many processes occurring naturally or induced artificially is generally known: in space and in the upper layers of the atmosphere, in radiation chemistry and photochemistry, in the pyrolysis of substances, in hydrogenation reactions, in plasmas, and in thermonuclear processes. There is reason to believe that organic substances are formed on the planets of the solar system as a result of reactions of hydrogen atoms[1].

There are several ways of obtaining hydrogen atoms (and the atoms of hydrogen isotopes—deuterium and tritium): thermal dissociation, electric discharge, photolysis, radiolysis, nuclear reactions, and an acceleration technique. In the thermal dissociation of molecular hydrogen, one obtains thermal atoms and, since the source region is at a high temperature, approximtely 10% of the atoms are obtained with an energy of approximately 0.3-0.5 eV.[2] In the remaining instances, hydrogen atoms have a non-equilibrium distribution. In an electric discharge there is a possibility of the formation of excited atoms[3]. Hydrogen atoms in certain quantum states are obtained by the electron impact method[4] or in a proton transfer reaction[5]. Hydrogen atoms appear when gas flows from an ultrasonic nozzle[6]. Owing to the dissociation of C—H bonds, the radiolysis of hydrogen-containing organic compounds results in the appearance of hydrogen atoms with an energy of 1—3 eV.[7] In photolytic experiments the energy of hydrogen atoms varies from 0.1 to 6 eV.[8] Recoil tritium atoms with energies of 0.19 and 2.7 MeV can be obtained by the nuclear reactions $^3He(n,p)^3H$ and $^6Li(n,\alpha)^3H$.[9] The technique of "chemical" accelerators makes it possible to obtain hydrogen atoms with energies in the range from approximately 1 to 200 eV [10] and to investigate the angular distribution of the reaction products[11]. Thus present day investigators are able to obtain hydrogen atoms with energies ranging from approximately 0 to 2.7 MeV. There is a prospect of investigating reactions with reactants having different energies and known quantum states.

According to the classical Arrhenius equation, with increase of temperature (collision energy) the probability of the reaction should tend to a value equal to the steric factor. However, if high-energy atoms are generated in the system, the reactions do not obey the Arrhenius kinetics; the steric factor increases[12] when the probability of the reaction depends in a complex manner on the collision energy[12,13]. Thus the reactions occurring at different relative collision energies cannot be described in terms of a single mechanism.

Ideas borrowed from collison physics and nuclear physics throw a significant light on the nature of chemical reactions. This concerns concepts such as the reaction cross-section and the excitation function. The cross-section of a chemical reaction reflects its probability for a specific quantum state of the initial reactants and final products, while the excitation function describes the dependence of the cross-section on the collision energy. By integrating over all possible states, one obtains the overall reaction cross-section and, on multiplying by the relative velocity of the reacting species, one finds the rate coefficient—a quantity analogous to the rate constant for a chemical reaction. For the equilibrium distribution of the reacting species with respect to energies, the rate coefficient is the rate constant for the chemical reaction.

Appreciable advances have been made in recent years in the study of the excitation functions $\sigma(E)$ of chemical reactions in general and of the reactions of hydrogen atoms in particular. The chemical reaction thresholds have been determined; it has been shown that $\sigma(E)$ corresponding to a specific energy has a maximum, beyond which it decreases to $\sigma(E) \cong 0$. Taking this into account, it is possible to classify the interactions of hydrogen atoms which are generated in some way in the medium in terms of their energies and the nature of their energy spectrum. If the spectrum is of the Boltzmann type, then usually only a small proportion of the atoms enter the region $E_1 \leq E \leq E_2$, where the function $\sigma(E)$ is determined. In this case the classical description based on the Arrhenius equation is entirely applicable in the region of "moderate" temperatures (200—500 K). At low temperatures quantum corrections for the wave properties exhibited by the hydrogen atoms are necessary, while at high temperatures account must be taken of the breakdown of the Boltzmann distribution as a consequence of the "burning away" of the active species.

If atoms with an energy in the region $E_1 \leq E \leq E_2$ are generated in the system where the function $\sigma(E)$ is determined (this is usually 0.1—10 eV) and if there is no equilibrium in the energy distribution of the atoms, then the Arrhenius equation is inapplicable to the description of the kinetics of the reactions of such species, which are referred to as "hot". The reaction can occur in the first collision and also subsequently when the atom has lost part of its energy, but subject to the condition that the residual energy of the atom lies within the limits of the region $E_1 \leq E \leq E_2$. If atoms with $E > E_2$ act on a given substance, then in the first collision the reaction is impossible and the atoms must be retarded until the energy is $\leq E_2$. Subsequently the reaction proceeds

in the same way as that with atoms generated in the range of energies $E_1 < E \leq E_2$.

The rate of a reaction involving species with an energy can be expressed by the general equation

$$w = \int_{E_1}^{E_2} p(E')\, n(E, E')\, \mathrm{d}E' \,, \qquad (1)$$

where $p(E')$ is the probability of the reaction for a collision energy $E = E'$ and $n(E,e')$ is the collision density (the number of collisions per unit time per unit volume). The collision density in the range of energies dE' near E' in general depends on the energy of the species E, falling within this range on retardation.

If $E > E_1$, the probability of the reaction of thermal atoms is assumed to be independent of the collision energy; the collision density is calculated from the Boltzmann distribution of the species with respect to energies. Hence it is possible to derive the Arrhenius law from Eqn.(1). For "hot" species, the assumption that the reaction probability is independent of the energy is invalid, because a considerable proportion of the species (if not all) have an energy $E \gg E_1$. However, in an analytical form, the $p(E)$ relation is as a rule unknown, so that the concept of integral probability is used in the solution of Eqn.(1) and the function $n(E,E')$ is found by solving the transport equation for the species with certain assumptions about the nature of the retardation process.

The advances in the chemistry of thermal hydrogen atoms described in Dubinskaya's[14] and Thrush's[15] reviews and the reactions of "hot" atoms considered in a number of other reviews[16-20] will be touched on in the present survey only where necessary. Attention is concentrated on new investigations and also on studies which had not been considered before.

II. REACTIONS OF THERMAL HYDROGEN ATOMS

1. Modern Ideas about the Reactivity of Thermal Hydrogen Atoms

The reactivity of hydrogen atoms has always been and still is the subject of extensive investigations. In view of its characteristic features—a light nucleus with a single electron—the hydrogen atom constitutes a system suitable for testing the validity of any physicochemical theory of reactivity and the existence of hydrogen isotopes permits the study of quantum and isotope effects in the kinetics of chemical reactions[21]. The commonest reaction of hydrogen atoms is of the type $A + BC \rightarrow AB + C$, i.e. a bimolecular substitution reaction (when C contains more than one atom, this is referred to as the abstraction reaction). The transition state (TS) theory has found the most extensive applications in the description of bimolecular reactions. A deficiency of this theory for atom—molecule reactions consists in the neglect of the tunnelling effect, which leads to unduly low calculated reaction rate constants at low temperatures. The "quantum-mechanical" rate constant is as a rule 1—2 orders of magnitude greater than the constant calculated on the basis of the TS theory[22].

The introduction of various corrections, as well as calculations by the method of trajectories, significantly improve the agreement between the classical and quantum-chemical calculations. A version based on a simple physical modification of the usual tunnel corrections is used, which consists in the fact that, instead of the movement of the representative point in the saddle area of the potential surface, one calculates its path along the curve connecting the classical turning points[23]. This leads to the narrowing of the calculated barrier to reaction compared with that obtained on moving along the potential energy maximum. This reaction pathway is shorter, which improves the agreement with quantum-mechanical calculations, for example, for reactions of the type

$$H + H_2 \rightarrow H_2 + H \,. \qquad (2)$$

However, in the study of the role of various corrections in the TS theory it has been shown that, although the Wigner relation usually employed has no rigorous theoretical proof, it is more consistent than any other for a wide set of reactions[23]. An attempt has been made[24] to take into account the vibrational non-adiabatic conditions in the abstraction reaction and the possibility of tunnelling within the framework of the TS quantum theory. It has been suggested that the "best" tunnelling path, common to all reactions, does not exist.

Tunnelling corrections are introduced as a rule within the framework of the "direct" mechanism of the TS theory: one considers the surface dividing the space of the reactant products in which there is a single trajectory of the movement of the representative point. This model is valid for energies which do not greatly exceed the threshold energy E_1. On the other hand, the majority of reactions proceed via the formation of a long-lived complex[25]. In the theory combining both concepts of bimolecular reactions (the "direct mechanism" and the "long-lived complex") expressions have been derived for the probability of reaction and it has been shown that they can be deduced from a general model[26]. The application of this model to the reaction between H and H_2 has been considered[27].

Starting from the 1950's the molecular orbital (MO) method began to be incorporated in chemical kinetics. A general approach based on the MO method to the abstraction reactions has been developed[28,29]. Here one uses concepts such as the stabilisation energy of the radical ΔE, the delocalisability D_r, and also the concept of the linear relation between E_a and ΔE:

$$E_a = A - B \cdot \Delta E; \; D_r = \sum_j (C_r^j)^2; \; \Delta E = C \cdot D_r$$

where C_r^j is the coefficient of the atomic orbital (AO) in the jth molecular orbital; the summation is carried out over all occupied and unoccupied MO: A, B, and C are constants.

If one considers a series of substances, for example, hydrocarbons, then the product of the abstraction reaction is H_2 and E_a should depend solely on the stabilisation energy of the radicals ΔE. The higher the stability of the radical obtained, the lower the activation energy for the reaction—a fact which has long been known in chemical kinetics[30]. However, it was not until the 1960's that it was possible to characterise the stability of chemicals quantitatively by introducing the concept of delocalisability[31], which was calculated by the MO method[31,32]. The value of the calculations lies in the accuracy and reliability of the evaluation of the coefficients of the AO. Approximate quantum-chemical methods are usually employed and only a qualitative correlation between E_a and $\Delta E(D_r)$ is obtained[31-33].

In general the MO method usually provides a description of the reactions at an adequately high qualitative level. Satisfactory results have been obtained by combining the MO method with the technique of correlation diagrams, whose construction is based on the principle of the conservation of orbital symmetry in the reaction[34]. The hydrogen abstraction reactions are symmetry-allowed and the reactivity of the C—H bond in various compounds with respect to the given reaction is determined by the electron density in the occupied and unoccupied MO of the initial molecules and by the delocalisation energy of the unpaired electron in the radical formed.

Correlation diagrams assist in understanding the course of the reaction. The abstraction reaction takes place in three stages[35]: in the first stage an electron is transferred from the RH molecule to a partially occupied orbital of the H atom and in the second stage an electron is transferred from the H atom to the lowest vacant orbital of the molecule (the spin-delocalisation stage). A charge is then accumulated in the region between the hydrogen atoms and the C–H bond is formed by the "local triplet" of two electrons, which is responsible for the dissociation of the C–H bond in the concluding, third reaction stage. The process described proceeds most readily under the conditions of an axial attack.

The application of the principle of conservation of orbital symmetry to the abstraction reaction does not account for the origin of the activation energy but makes it possible to understand certain details of the formation and dissociation of the bonds. A more general principle of the description of chemical reactions, consisting in the fact that the reaction is regarded as allowed if the distortions occurring on a given pathway do not give rise to new nodal planes in the wave functions, has now been proposed. The principle of the conservation of orbital symmetry is a special case of a more general principle[36]. The fundamental feature of the proposed analysis of the reactions is the introduction of an operator which satisfies the requirements of the prohibition of a change in nodal structure (mapping operator). The reaction is allowed if the mapping function and the wave function of the putative product overlap.

Some investigators have developed an even more general approach to the study of the kinetics of chemical reactions[37–39]. On the basis of the general principles of wave mechanics, they assume that the probability of the reaction is proportional to the overlap integral of the wave functions of the initial and final states of the species. There is then no need to consider the usual reaction path as the movement of a point on the potential energy surface, to construct correlation diagrams, and to introduce corrections for reactions via other mechanisms, for example the tunnelling mechanism: within the framework of the proposed theory, the tunnelling process is inherently included. The conclusion that heat is evolved in an exothermic reaction mainly in the form of the internal energy of molecules is one of the consequences of the wave theory of chemical reactions, which has been confirmed experimentally.

2. The Reactions of Hydrogen Atoms with Inorganic Substances

An enormous number of studies have been made on reaction (2) and its isotopic variants. One of the latest reviews[21] considers the application of the collision theory to the activated complex theory taking into account the quantum and isotope effects. The reaction dynamics have been considered in a review[40] as a consequence of trajectory calculations. Quantum-mechanical calculations have been made on the cross-sections of reaction collisions and the differential cross-sections. the reaction threshold. and the quantum state of the products have been evaluated. Theoretical studies are usually preformed on the basis of a variant of the TS theory taking into account tunnelling effects at temperatures $T < 450$ K. A satisfactory agreement with experiment is then achieved[41]. Thus the isotope effects of the reactions between D and H_2 and between H and D_2 have been calculated[42] for the range 200–4000 K. An analogous study has been made for the reactions between H and H_2 and between D and D_2.[43]

Quantum-chemical calculations make it possible to calculate the reaction thresholds and to consider the reaction dynamics and the population of the states of the products. A three-dimensional quantum-chemical study has been made[44] of the reaction $D + H_2 \rightarrow HD + H$; the reaction threshold was estimated as 0.27 ev (which virtually agrees with experiment) and intense back-scattering (ricochet) and population of the lowest levels of the HD molecule were predicted.

Reactions of the type $X + H_2 \rightarrow$ and $H + X_2 \rightarrow$, where X = H, D, or ^3H, have been investigated by the method of classical trajectories for collinear collisions and for the three-dimensional case[45]. In the first case the reaction thresholds for different isotopes differ little (0.27–0.28 eV), but in the second case the differences are significant (for the reactions of H atoms with H_2, D_2, and $^3H_2$, the thresholds are 0.271, 0.192, and 0.157 eV respectively). The calculations showed that between 0.3 and 0.45 of the collision energy is converted into the internal energy of the product. It is of interest to note that the differences in the reactivity, which are usually attributed to thermal effects, are accounted for in this instance by simple dynamic effects on collision between the species.

A detailed experimental study of the reactions of hydrogen atoms with hydrogen molecules (and the molecules of its isotopes) has been made by the usual thermal techniques. However, only studies in beams make it possible to obtain information about the fine details of the reaction mechanisms and to answer the questions which modern theories of reactivity cannot answer. In connection with apparatus difficulties, only as late as 1970 was it shown that HD, the product of the reaction between D and H_2, is scatterd "backwards" in the centre of mass system and that the internal excitation of molecules is low[46]. Since hitherto it has not been possible to overcome the difficulties associated with the experiments in beams, particularly in the detection of products, it has been suggested that the reactions of hydrogen atoms with tritium molecules, i.e. $X + {}^3H_2 \rightarrow$ (X = H or D), be investigated with detection of the products on the basis of their radioactivity[47]. The forward scattering of tritium atoms in the reaction

$$H + {}^3H_2 \rightarrow H^3H + {}^3H$$

and the back-scattering of H^3H molecules were observed, i.e. the direct abstraction reaction was noted. The above report[47] contains valuable information about the angular distribution of products, but there are no data on the distribution with respect to velocities, which precludes any conclusions concerning the form of the potential energy surface.

At ultralow temperatures the hydrogen atoms in the molecular hydrogen matrix are stabilised[48] and at $T < 1$K an average concentration of hydrogen atoms of 0.01% was attained. Since the radicals were obtained in solid H_2 with the aid of the β-decomposition of ^3H, the local concentration [H] was much higher. The temperature T_R at which the H_2 specimen containing H atoms becomes unstable and spontaneous (or stimulated) evolution of energy takes place has been found. It has been noted that T_R decreases with increasing storage time of the specimens. The authors[48] concluded that the regions of a high concentration of H atoms behave similarly to ferromagnetic domains. Subsequently a study was made of the kinetics of the accumulation of hydrogen atoms in solid H_2 containing 2% $^3H_2$ at $T < 1$ K.[49] Hydrogen atoms are stabilised by the reactions

$$H + {}^3H_2 \rightarrow H^3 \cdot H_2 \quad \text{and} \quad H + H^3H \rightarrow H_2 \cdot {}^3H.$$

It was found that at $T \cong 0.17$ K the limiting concentration is $[H] \cong 5 \times 10^{19}$ atoms cm^{-3} or 2×10^{-3}M, i.e. a high concentration of hydrogen atoms is not reached.

A study of reactions of the type $H + X_2 \rightarrow$ (X = halogen) by methods of classical and quantum mechanics showed that the main discrepancy between their results occurs near the threshold owing to the neglect of the contribution of complex trajectories in the classical treatment of the reaction pathway[50,51]. The classical description with a more "accurate" treatment of the region of the threshold (for example with optimisation of the transition state) gives rise to a good agreement of the rate constants with experimental values for the reactions of hydrogen atoms with HBr, ^{3}HBr, F_2, and Cl_2.[52] The "accurate" treatment consisted in employing in the calculations two dividing surfaces: one for energies less than the energy at the saddle point and the other for higher energies.

Modern experimental data (vibrational excitation of products, rate constants, rate constant ratios, angular distribution) permit the calculation of parameters characterising the potential energy surface, for example, for the reaction between D(H) and X_2, where X = Cl or muonium[53]. In certain cases the same reaction products can be obtained via different channels, for example:

$$H + XY \begin{cases} \longrightarrow H\cdots XY \rightarrow HX + Y & (3) \\ \longrightarrow X{-}Y \rightarrow HX + Y \\ \quad\vdots \\ \quad H & (4) \end{cases}$$

Reaction (3) proceeds via the "direct" mechanism and reaction (4) involves the insertion mechanism. Theoretical study showed that the probability of reaction (3) increases and that of reaction (4) falls with increasing translational energy of the hydrogen atom[54].

A few studies of the interaction of hydrogen atoms with inorganic compounds have been described in the literature. Langmuir was the first to show[55] that atomic hydrogen reacts with phosphorus and reaction parameters have been given in a review[56] †:

$$H + NO_2 \xrightarrow{k} OH + NO, \quad \Delta H^0_{298} = 122 \text{ kJ mol}^{-1}, \quad k_{300} = 2\cdot 10^{13} \text{ cm}^3 \text{ s}^{-1} \text{ mol}^{-1};$$

$$H + ClNO \xrightarrow{k'} HCl + NO, \quad \Delta H^0_{298} = -273 \text{ kJ mol}^{-1}, \quad k' \simeq k.$$

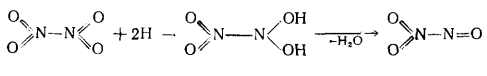
The addtion of H atoms to O_2 and NO_2 has been considered[57] and the rate constants for the reactions of H and D atoms with NO_2, N_2H_4, Cl_2, NOCl, HBr, and DBr in the range 200–700 K have been published[58–62].

In the reaction of hydrogen atoms with carbon[63] in the range 300–1220 K the formation of CH_4 (91%), C_2H_6 (8.4%), C_3H_8 (0.6%), and secondary products (C_2H_4, C_3H_6, and C_4 hydrocarbons) has been observed[63]. With increase of temperature, the yield of hydrocarbons rose and the temperature dependence of the yield of CH_4 revealed three stages of the reaction, for which the activation energies were found: 4.5 ± 1.2, 0.15 ± 0.05 and 0.94 ± 0.20 kcal mol^{-1} for the temperature ranges 1000–1200, 500–1000, and 300–500 K respectively. At 300 K approximately 1% of hydrogen atoms interact with carbon, being converted into hydrocarbons; at 1220 K this fraction reaches 4%. Methane, being the primary reaction product, can probably react further with atomic hydrogen to form other hydrocarbons[54].

On interaction of hydrogen (and deuterium) atoms with solid N_2O_4 at 77–100 K, the following reaction was observed[65]:

$$N_2O_4 + 2H \rightarrow N_2O_3 + H_2O .$$

The authors[65] believed that the preferred mechanism of the reaction involves the reduction of nitrogen:



† Here and henceforth the units of energy are given in the same way as in the original communications.

Interesting studies have been made on the interaction of hydrogen atoms with cobalt(III) and copper(II) complexes[66]. It has been shown that for cobalt compounds the reduction of the complex-forming agent is preceded by a stage involving the dehydrogenation of the coordinated ligand. The reaction results in the formation of molecular hydrogen and a coordinated radical, which reduces cobalt(III) to cobalt(II) at the instant of its formation. The reduction of copper(II) in its complexes with aminoacids, which may be regarded as square-planar compounds, proceeds via an intermediate stage in which a hydride complex is formed, omitting the dehydrogenation of the coordinated ligand:

$$R_2 \,|\, Cu\,(II) \,|\, + H \rightarrow R_2 \,|\, Cu\overset{H}{\diagup}\,(II) \,|\, \rightarrow H^+ + R_2 \,|\, Cu\,(I) \,|\, \rightarrow R^- + R{-}Cu\,(I)\,,$$

where R is the aminoacid residue. As was to be expected, the rate constant for this reaction is independent of the chemical nature of the coordinated residues (glycine, alanine, and valine).

Since targets made up of substances subjected to the action of atomic hydrogen are as a rule deposited on glass, the interaction of glass with hydrogen atoms is of particular interest. Langmuir showed[55] that the rate of absorption of hydrogen by glass depends on the temperature of the source of atoms—a heated tungsten spiral, on the purity of the surface of the glass, and on its temperature. Later it was demonstrated[67] that only atomic hydrogen is absorbed; the absorption takes place at a temperature of the source of atoms ≥1300 K and only when the glass is cooled to 80 K. After heating the glass, the atoms recombine and the hydrogen is partly removed from its surface. Since repeated cooling of the glass (without atomisation) does not alter the hydrogen pressure, it follows that molecular hydrogen is desorbed. The H_2O, CO_2, and O_2 impurities are always present on the surface of the glass and prevent the adsorption of atomic hydrogen, being fully removed only after prolonged heating at approximately 600 K. The maximum number of atoms is approximately 1.5×10^{15} atoms cm^{-2},[55] while the number of tritium atoms on molybdenum glass is approximately 1×10^{16} atoms cm^{-2}, the sorption on glass being accompanied by the exchange of tritium for protium[68].

It has been found[69] that hydrogen atoms populate two states. The first state ($E_a = 25$ kcal mol^{-1}) is characterised by the formation of chemical bonds on the surface of the glass. The second rate ($E_a = 6.6$ kcal mol^{-1}) is determined by the van der Waals forces retaining the hydrogen atoms near the chemisorbed atoms. The populations of the two states are approximately the same. The rate of capture of thermal hydrogen atoms by Pyrex glass at 77 K and an initial hydrogen pressure of 5×10^{-2} mmHg is 2.8×10^{15} atoms cm^{-2} s^{-1}.[69] The adsorption of hydrogen atoms on zeolites depends greatly on the amount of water adsorbed on the surface[70], which can apparently be accounted for by the stabilisation of atoms on the acid surface centres. It may be that an analogous process also occurs on glass. Indeed the rate of capture of hydrogen atoms by glass differs by a factor of four for dry and wet surfaces[68].

In general the method of preliminary treatment of the surface has a major influence on the adsorption properties of the glass. The process is characterised in terms of the concept of the "recombination coefficient" γ, which is equal to the ratio of the number of atoms recombining on the surface to the total number of atoms impinging against the surface during the same period[71]. With increase of the temperature, we have $\gamma \rightarrow 1$.[15] Treatment of the glass with hydrofluoric or phosphoric acid reduces the value of γ.[72,73].

Treatment with acid apparently leads to an increase in the concentration of adsorbed atoms existing in a chemical state such that the atoms are incapable of impact recombination[68]. These conclusions have been confirmed by EPR data for the chemical state of sorbed hydrogen atoms. It has been found[72] that, as a result of sorption, the electron of the hydrogen atom is partly transferred to the *p* orbital, i.e. the properties of the sorbed species are altered (for example, the electrical properties of the solid phase, as a consequence of electron transfer to the valence band[74]). When tritium is used, this can be manifested by isotope exchange between ^3H and the molecules of substances containing "labile" hydrogen atoms[68,75].

Among reactions of hydrogen atoms with metals, the most detailed studies have been made of those with silver films on glass[76], the adsorption of hydrogen atoms on silver proceeding without an activation energy, and with sodium films at 78–178 K,[77] where low activation energies were observed. The efficiencies of the adsorption on palladium[78] of hydrogen atoms obtained in an electric discharge and by thermal dissociation have been compared. In the latter case a high efficiency was achieved and the ratio H/Pd was approximately 0.9, while the activation energy for the sorption of hydrogen by palladium proved to be 26.8 kcal mol^{-1}.

Qualitative conclusions have also been reached concerning the rates of reaction of hydrogen with COS, HN_3, and with a whole series of metals (Li, Na, Hg, Gd, Ga, Ca, Ba, Bi, Zn, Cu, and Mg) on the basis of observations of the changes in the hydrogen pressure in the system[79], but little information can be derived from these data.

It is of interest to use hydrogen atoms to investigate the surfaces of crystals[80]. The scattering from LiF crystals has been studied with the aid of monochromatic atoms. The Debye–Waller factor and the force parameter of the Morse function have been calculated from experimental data.

3. Reactions of Hydrogen Atoms with Organic Substances

(*a*) *Saturated aliphatic and cyclic hydrocarbons.* Theoretical studies on the reactions of hydrogen atoms have usually been made for the simplest hydrocarbon (methane) and in quantum-chemical calculations account has been taken of the polarisation of wave functions[81], which leads to a better agreement with experiment than the use of the London–Eyring–Polanyi–Sato (LEPS) potential[82]. The hydrogen abstraction reaction is believed to occur in a collinear collision and the exchange (substitution) is thought to proceed via a "trigonal bipyramidal" complex[81]. Since the latter process has $E_{thresh} \cong 35$ kcal mol^{-1}, it can only be induced by "hot" atoms. Theoretical studies on reactions with other hydrocarbons are limited by the possibilities of modern methods: in essence there have only been calculations by the MO method using the relation between the activation energy and certain reactivity indices, for example delocalisability[31–33].

The reactions of thermal hydrogen atoms with hydrocarbons may involve a process leading to the exchange of atoms but not via a single-stage substitution mechanism, involving instead consecutive abstraction and recombination reactions. Such reactions can be followed with the aid of an isotope technique. Apparently Shores and Moser[83] were the first to show that thermal tritium atoms can interact with saturated compounds such as n-hexane and cyclohexane. The kinetics of these reactions have not been studied and the reaction products have not been identified. The abstraction of a hydrogen atom from isobutane has been demonstrated[84].

The effect of thermal tritium atoms on propane has been studied in greater detail[85]. The activation energy for the reaction

$$H + C_3H_8 \rightarrow H_2 + C_3H_7^{\cdot}$$

is 7.1 kcal mol^{-1} at 480 K [86] and diminishes somewhat with decrease of temperature as a consequence of the different temperature dependences of the rates of reaction of hydrogen atoms with the CH_3 and CH_2 groups of propane. [^{3}H] propane can be formed as a result of a two-stage process—the formation of the propyl radical and its subsequent recombination, for which less energetic atoms are responsible, and also as a result of the direct substitution of hydrogen by tritium. The mechanism of the formation of side products, among which methane, ethane, ethylene, and propene have been found, can be represented schematically as follows:

$$H + C_3H_7^{\cdot} \rightarrow CH_3^{\cdot} + C_2H_5^{\cdot},$$
$$H + C_2H_5^{\cdot} \rightarrow 2CH_3^{\cdot},$$
$$H + CH_3^{\cdot} + A \rightarrow CH_4 + A \text{ etc.},$$

i.e. the rupture of C–C bonds in the radicals on collision of the latter with thermal hydrogen atoms is apparently possible. In addition one must take into account the occurrence of rapid substitution (exchange) reactions leading to the preferential rupture of secondary C–^{3}H bonds in alkanes[87].

The primary reaction of hydrogen atoms with cyclopropane[88] is the abstraction of hydrogen with formation of the cyclopropyl radical, the subsequent addition of hydrogen to which results in the formation of excited cyclopropane molecules. The excited molecules isomerise with formation of propene. Since the excitation energy after the addition of a hydrogen atom to the cyclopropyl radical is greater by approximately 35 kcal than the activation energy for the isomerisation of cyclopropane to propene, the probability of this process is fairly high.

The abstraction reaction has also been observed in the interaction of a stream of hydrogen atoms at a temperature of 2000 K with a cyclohexane target at 77 K; the activation energy for the abstraction of hydrogen was 6–8 kcal mol^{-1}.[89] This is the primary reaction and is followed by a disproportionation reaction (between a tritium atom and a cyclohexyl radical) with formation of cyclohexane, the addition of a tritium atom to which accounts for the appearance of labelled cyclohexyl radicals in subsequent processes. When the target is heated, the reactions of cyclohexyl radicals—disproportionation, recombination, and addition to a double bond—occur near the polymorphic transition temperature (160–190 K), which can be explained by the self-diffusion occurring near the phase transition temperatures[90]. The ratio of the disproportionation and recombination rate constants (k_{dispr} and k_{rec} respectively) for the cyclohexyl radicals at 77 K is approximately 5 ± 1, while E_a(rec.)–E_a(dispr.) $\cong$ 300–400 cal mol^{-1}. In a study of the temperature dependence of the destruction of cyclohexyl radicals in the range 70–145 K, it was found[91] that the yield of bicyclohexyl increases with increase of temperature, the increase being sharp as the phase transition temperature of cyclohexene is traversed and $k_{dispr}/k_{rec} \propto T^{-5.1}$. It has been suggested[91] that the "heating" of the molecular movement in the phase transition is manifested most effectively in the radical recombination reaction.

It is of interest that a high reactivity in the hydrogen abstraction reactions has been observed for a series of silanes [SiH_4, Si_2H_6, CH_3SiH_3, $(CH_3)_2SiH_2$] compared with the hydrogen analogoues[92,93]. Apparently the difference can be accounted for by the difference between the activation energies, since the pre-exponential factors are similar in the two cases and the decrease of the activation energy corresponds to the decrease of the Si–H bond energy.

(*b*) *Unsaturated hydrocarbons.* There have been few theoretical studies on the reactions of hydrogen atoms with unsaturated compounds. As a rule, they are confined to an examination of correlations between the rate constants and reactivity indices, for example, the localisation energy, calculated by simple MO methods. The height of the barrier to the reaction involving the addition of a hydrogen atom to ethylene has been calculated only recently by the Hartree–Fock method with optimisation of the geometry. The calculated barrier (5.1 kcal mol^{-1}) is close to the experimental value[94].

A number of investigators have proposed mechanisms of the possible reactions, devised by analysing the products of the reactions of hydrogen atoms with hydrocarbons, and also reaction parameters and EPR data[95–105]. These mechanisms have many features in common: in the first stage the hydrogen atom addition process results in the formation of radicals[96,104], which is followed by rapid secondary reactions—the disproportionation and recombination of the radicals with one another or with hydrogen atoms and, in the case of deuterium and tritium atoms, disproportionation and recombination of mixed radical species take place. Furthermore, in virtually all cases dimerisation reactions are observed, but the relative rate of the latter is low. For example, the ratio of the amount of propane obtained in the reaction of hydrogen atoms with propene to the amount of the dimerisation product (2,3-dimethylbutane) is approximately 9,[105] while the ratio to the total amount of all the hexane isomers obtained is approximately 11.[103]

For hydrocarbons with a carbon chain longer than that of propene, account must be taken of specific reactions associated with the position of the double bond. For example, a shift of the double bond with formation of *trans*-but-2-ene is characteristic of the reactions of hydrogen atoms with but-1-ene. The reactions of hydrogen atoms with buta-1,2-diene and buta-1,3-diene lead to different final products, since the addition of hydrogen to buta-1,3-diene can involve either double bond, while the "non-terminal" addition to buta-1,2-diene is energetically unfavourable, which leads to the formation of but-2-ene as the main product.

In the deuteration of a solid olefin there is a possibility of H–D exchange between the hydrogen atoms and the free alkyl radicals[106,107]:

$$\dot{R}_H + D \rightarrow \dot{R}_{(D)} + H \ .$$

On passing to unsaturated cyclic compounds, the same features are observed as for olefins. Thus, when tritium atoms reacted with cyclohexene[108], an addition reaction was observed and cyclohexane, cyclohexene, and bicyclohexyl, obtained as a result of consecutive recombination–disproportionation reactions, were found among the labelled reaction products. At low temperatures the rate constant for the recombination reaction is lower than that for the disproportionation reaction, but k_{rec} increases faster than k_{dispr} with increase of temperature. The activation energy for the addition of hydrogen atoms to cyclohexene is approximately 1.5–3.5 kcal mol^{-1},[108] which is consistent with the calculation based on the Semenov–Polanyi rule.

When tritium atoms were allowed to react with cyclohexylcyclohexene isomers, the formation of isomeric compounds together with hydrogenation products was observed. Furthermore, the proportions of the products and the ratios k_{dispr}/k_{rec} depend on the nature of the solvent, i.e. are related to the different rigidities of the maxtrix[109].

(*c*) *Compounds containing functional groups.* In the reactions of hydrogen atoms with alcohols the main process is the abstraction of hydrogen from the carbon atom in the α-position relative to the OH group and the subsequent formation of alkanes and aldehydes[110–112]:

$$H + CH_3OH \rightarrow H_2 + \dot{C}H_2OH \xrightarrow{H} \dot{C}H_3 + OH \ ;$$

$$H + CH_3CH_2OH \begin{cases} \rightarrow H_2O + C_2H_5 \xrightarrow{H} C_2H_6^* \rightarrow 2CH_3 \begin{cases} \rightarrow C_2H_6 \\ \xrightarrow{H} CH_4 \end{cases} ; \\ \rightarrow CH_3\dot{C}HOH + H_2 \begin{cases} \xrightarrow{H} CH_3CHO \\ \xrightarrow{H} CH_3\dot{C}H \rightarrow C_2H_4 \end{cases} ; \end{cases}$$

$$H(D) + CH_2{=}CHCH_2OH \rightarrow CH_2{=}C\dot{H}CHOH + H_2\ (HD) \ .$$

t-Butyl alcohol, where the abstraction of the OH group is the dominant process, constitutes an exception. The rate constants for the primary reactions are presented in Table 1. The secondary reactions are determined by the nature of the radical obtained. Thus the addition reaction with formation of propanol and propionaldehyde predominates for allyl alcohol.

Table 1. The rate constants for the reactions of hydrogen atoms with aliphatic alcohols [$k = A \exp(E/RT)$].

Alcohol	A, $cm^3\ s^{-1}\ mol^{-1}$	E, cal mol^{-1}	References
CH_3OH	$6.5 \cdot 10^{12}$	5440±150	[110]
	$1.3 \cdot 10^{13}$	5260	[212]
C_2H_5OH	$(4.2 \pm 0.4) \cdot 10^{19}$	4200±300	[112]
$(CH_3)_3COH$	$(4.0 \pm 0.4) \cdot 10^{13}$	8200±650	[112]

The mechanism of the reaction of hydrogen atoms with dimethyl ether has been published[110]:

$$H + CH_3OCH_3 \rightarrow \dot{C}H_2OCH_3 + H_2$$

$$CH_3OCH_3^* \xrightarrow{H} \rightarrow \dot{C}H_3 + \dot{O}CH_3 \begin{cases} \rightarrow CH_2O + H_2 \\ \rightarrow \dot{C}H_3 + OH \end{cases} .$$

According to the authors, the identity of the activation energies for this reaction and the reaction of atomic hydrogen with CH_3OH indicates the similarity of the mechanisms of these processes.

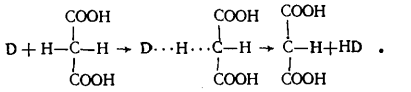
A characteristic reaction of hydrogen atoms with nitrocompounds (nitromethane, nitrobenzene, nitroethylene, and nitroisopropene) is the addition of a hydrogen atom to the nitro-group.

$$H + R{-}N\begin{matrix}O\\O\end{matrix} \rightarrow R{-}\dot{N}\begin{matrix}O\\OH\end{matrix} \ ,$$

which is a more effective hydrogen atom acceptor than the benzene ring and the C=C bond[113]. The NCO and NCS groups also effectively capture hydrogen atoms and the mode of reaction in this instance depends significantly on the nature and position of the subsequent substituent (if such exists) relative to the NCO (NCS) group. Thus a hydrogen atom adds to the benzene ring of phenyl isocyanate, but, after the introduction of a second functional group into the latter (CH_3, NO_2, $OCNC_6H_4CH_2$), the double bond of the NCO or NO_2 groups is attacked[113], since the second substituent alters significantly the distribution of electron density in the molecule.

When malonic and methylmalonic acids react with thermal hydrogen atoms, the C–H bond is ruptured, the dissociation of a carbon–carbon bond is not observed[114,115], and the

hydrogen atom of the methylene group is abstracted:



A similar reaction is characteristic also of malonamides.

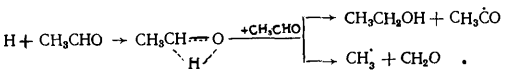
If the initial acid contains double bonds, the latter are hydrogenated. For example, it has been observed that the main process in the reaction involving oleic acid[116] is the formation of stearic acid and the ratio of the contributions of the addition and substitution reactions was approximately 2.6.

The reaction of atomic hydrogen with aldehydes proceeds in the same way as for carboxylic acids, i.e. involves the abstraction of a methylene hydrogen atom, which leads to the formation of keten, methane, ethane, and carbon monoxide[117]:

$$\begin{gathered}
H + CH_3CHO \xrightarrow{k_1} CH_3\dot{C}O + H_2 \ , \\
CH_3\dot{C}O + H \begin{cases} \xrightarrow{k_2} CH_3 + CHO \\ \xrightarrow{k_3} CH_2CO + H_2 \end{cases} , \\
CHO + H \rightarrow CO + H_2 \ , \\
H + CH_3 + A \rightarrow CH_4 + A \ , \\
2CH_3 \rightarrow C_2H_6 \ , \\
H + CH_2CO \rightarrow CH_3 + CO \ ,
\end{gathered}$$

where $k_2/k_3 \cong 4.7$ and $k_1 = (2.6 \pm 0.2) \times 10^{12} \exp(-2600/RT)$ is close to the corresponding rate constant for the reaction of atomic hydrogen with methanol.

Virtually none of the communications concerning the action of atomic hydrogen on compounds containing the carbonyl group provides information about the addition of hydrogen atoms to the C=O bond. An impression has been created that the C=O bond differs so much from the C=C bond that the addition reaction is impossible. Only recently[118], in a study of the reactions between atomic hydrogen and acetaldehyde, was ethanol detected as the reduction product. To account for its formation, the authors[118] proposed the following mechanism:



The excess energy evolved in the addition of hydrogen (21 kcal mol^{-1}) is sufficient for the occurrence of the above reactions.

When tritium atoms act on $C_5H_{11}X$ (X = SH, NH_2, OH, or COOH) at 77 K, pentane is formed, whose tritium content is correlated with the bond energies of the substituents[119].

(d) Aromatic and Heterocyclic compounds. When thermal hydrogen atoms react with aromatic compounds, the main reaction is the addition of a hydrogen atom to the benzene ring with formation of radicals of the cyclohexadienyl type[120]. Such reactions have been observed for a large number of substances[121-127], but in many instances the competitive abstraction of a hydrogen atom from the substituent or its addition to the C=C bond of the side chain takes place. For halogenotoluenes, the rate constant for the abstraction of a benzyl hydrogen atom is close to the value determined by diffusion[128].

The rates of abstraction reactions involving mesitylene, tetralin, phenylcyclohexane, and thiophenol are comparable to the rate of addition to the benzene ring and, in the case of phenol and benzyl alcohol, the abstraction of the OH group takes place together with addition to the benzene ring:

$$R{-}OH + H \rightarrow R^{\cdot} + H_2O \ .$$

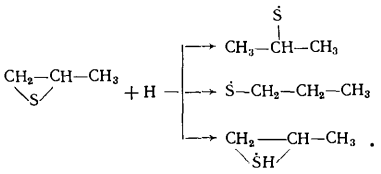
The difference between the activation energies for the abstraction and addition reactions is 0.5 kcal mol^{-1}.[129] For aniline and benzyl chloride, the abstraction reactions are the main processes, while in the case of nitrobenzene and nitrosobenzene the reactions involving addition to the ring are not observed at all. Hydrogen atoms add almost completely to the N=O bond.[123]

When hydrogen atoms attack the side group, π-electron radicals are formed in which there is resonance interaction, according to EPR data, of the unshared electron with the π-electron system of the ring (phenol, which gives rise to σ-radicals, is an exception).

The kinetics of the accumulation of radicals are described satisfactorily in this case by a model taking into account the diffusion of hydrogen atoms from the gas phase to the solid phase and the occurrence of a first-order chemical reaction[97]. The low rate of accumulation of radicals observed for a series of substituted benzenes (amines and alcohols) compared with benzene is apparently associated with the fact that in these substances the diffusion coefficient of hydrogen atoms is low owing to the presence of hydrogen bonds[130].

When tritium atoms react with benzene at 77 K, ≤5% of the labelled parent compound is formed, while the remaining products are hydrogenation products, mainly [^{3}H] cyclohexene, which indicates a low rate of the disproportionation reaction[131]. Under the same conditions, considerable amounts of [^{3}H] toluene are formed from toluene[132]. In the reactions with benzene derivatives there is a possibility of the substitution of functional groups[133].

For heteroaromatic compounds, the same processes have been observed as for aromatic systems, i.e. the addition of a hydrogen atom to the unsaturated bonds in the ring[134]. For certain sulphur compounds, for example, methylthiiran, the addition of a hydrogen atom to the sulphur heteroatom has been observed[135]:



In the general case the dissociation of the C–H bond in the α-position relative to the heteroatom is characteristic of saturated heterocyclic compounds[126,135].

(e) Polymers. Substances of this class react with hydrogen atoms either with abstraction of hydrogen from the saturated molecules or via addition to the benzene ring, for example, in polystyrene[136], polymethylstyrene, and poly(ethylene terephthalate)[137,138]. Data for radicals detected by EPR in high-molecular-weight compounds have been examined in detail in two studies[139,140].

The activation energies for the abstraction of a hydrogen atom from the main polymer chain are, for example 2 and 1.2 kcal mol^{-1} for the reactions involving polyisobutylene and poly(ethylene oxide) respectively at 100–150 K and the temperature dependence of the rate constants does not obey the Arrhenius law[134]. These facts were explained by the considerable contribution of the tunnel transfer of hydrogen atoms to the rate of the process[141].

(f) Biologically active substances. The interaction of hydrogen atoms with biologically active compounds has been little studied. Moser and coworkers[75] were the first to obtain labelled sucrose, glucose, and starch by acting on frozen targets with "heated" tritium atoms. The reaction is believed to proceed in two stages: with abstraction of a hydrogen atom and subsequent recombination with a tritium atom. The same method has been used to obtain [^{3}H] alanine[142] and [^{3}H] ribonuclease[143] with a fairly high specific activity. Tritium-labelled adrenocorticotropin[144], morphine[145], and valine[116] with specific activities of 15, 2.7, and 3 mc mmol^{-1} respectively and certain peptides[146] have been obtained under the conditions of a microwave discharge. [^{3}H] ribonuclease with a specific activity of 1.5–3.5 mc mmol^{-1} has been obtained under conditions where tritium atoms were generated in a silent electric discharge[147]. A high specific activity of biologically active compounds can be achieved using an arc discharge[148].

The complexity of the study of the mechanism of the interaction of hydrogen atoms with biological objects consists primarily in the presence in the latter of numerous functional groups and also of secondary and tertiary structures in proteins. The steric factor plays here a significant role and the conclusion that such reactions occur on the surfaces of large molecules is particularly important in this connection[75, 115].

The formation of radicals from aminoacids (Table 2) is associated, as usual, with abstraction of hydrogen atoms from saturated molecules and their addition to unsaturated and aromatic molecules. However, the hydrogenation of aromatic bonds in the ring is negligible for phenylalanine[116], although radicals of the cyclohexadienyl type have been detected in reactions of atomic hydrogen with aromatic aminoacids (phenylalanine, tyrosine, and tryptophan)[149]. For proline, ring opening has been noted[150]. Furthermore, there is a possibility of deamination (and decarboxylation) processes associated with the addition of hydrogen atoms to the amino-group[142] (or with formation of radicals of the type $R-\dot{C}(=O^-)-OH$, which can be stabilised by protonation[151]).

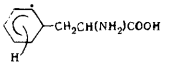
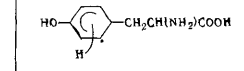
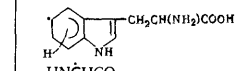
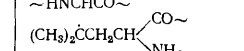
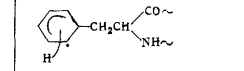
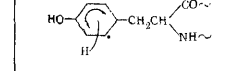
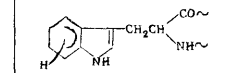
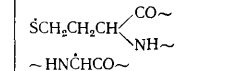
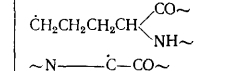
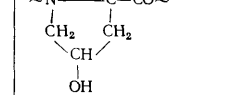
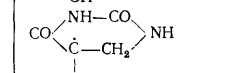
The action of hydrogen atoms on the peptide bond, leading to the formation of molecular fragments with a lower molecular weight, is important for polyaminoacids. The presence of aromatic aminoacid molecules in the chain leads to a greater stability of the polypeptide[152].

An important but little investigated process is the intramolecular distribution of tritium in labelled molecules obtained on treatment with tritium atoms. The α-, β-, and γ-positions in [^{3}H] valine contain 7.1, 32.7, and 60.2% of tritium respectively[116]. The predominant concentration of tritium in the β-position has also been observed in labelled L-isoleucine and L-alloleucine[152], which is due to differences between the bond energies and the activation energies for the abstraction of hydrogen from different positions in the molecule. In the cleavage of [^{3}H] ribonuclease[147] into individual aminoacids, the greatest proportion of tritium was found in methionine, glycine, and histidine, while the tritium content in threonine, serine, and arginine proved to be insignificant.

Apart from labelled parent compounds, products resulting from deamination, carboxylation, and the abstraction of the OH group, with a high specific activity, have been detected in the interaction of tritium atoms (0–0.2 eV), obtained by the thermal dissociation method, with aromatic aminoacids (tyrosine and phenylalanine)[154].

Tritium atoms with an average energy of approximately 0.02 eV mainly abstract hydrogen atoms from the β-position in the side chains of phenylalanine and tyrosine[155,156] which agrees qualitatively with calculations by the MO method[157,158].

Table 2. The radicals formed in the interaction of hydrogen atoms with certain biologically active compounds.

Compound	T, K	Radical	References
Glycine	298	$^+H_3N\dot{C}HCOOH$	[152]
Alanine	298	$CH_3\dot{C}HCOOH$	[152]
Leucine	298	$(CH_3)_2\dot{C}CH_2CH(NH_2)COOH$	[152]
Phenylalanine	77–300		[149]
Tyrosine	77–300		[149]
Tryptophan	77–300		[149]
Polyglycine	77–300	$\sim HN\dot{C}HCO\sim$	[150]
Polyalanine	77	$CH_3\dot{C}HCO\sim$	[150]
Poly-DL-alanine	77	$\sim HN\dot{C}(CH_3)CO\sim$	[150]
Poly-L-serine	77	$\sim HN\dot{C}HCO\sim$	[150]
Poly-DL-leucine	77–300		[150]
Poly-L-phenylalanine	77–300		[149]
Poly-L-tyrosine	77–300		[149]
Poly-DL-tryptophan	77–300		[149]
Poly-L-methionine	77		[150]
Poly-L-lysine	77	$\sim HN\dot{C}HCO\sim$	[150]
Poly-L-proline	77–300		[150]
Poly-L-hydroxyproline	77–300		[150]
Thymine, dihydrothymine	160–300		[153]
Penicillamine	160–300	$HOCOCH(NH_2)C(CH_3)_2\dot{S}$	[115]

In the temperature range 30–200 K tritium atoms also react with aminoacids and the experimental activation energies for these reactions are close to zero and below 60 K the limit of the chemical reaction rate is reached[156,159]. This makes it possible to suggest the occurrence of tunnel reactions and to estimate the parameters of the barrier. The probabilities of reactions involving the abstraction of hydrogen from different aminoacids by tritium atoms at 300 K have been compared[160] with the reactivity indices—the boundary electron density and delocalisability, a satisfactory qualitative agreement being found.

III. REACTIONS OF "HOT" HYDROGEN ATOMS

1. Models of Chemical Reactions Involving "Hot" Hydrogen Atoms

Theoretical studies of the reactions of atoms having an excess of kinetic energy have developed in two directions. On the one hand, attempts have been made to relate the yields of reactions to the characteristics of the moderation process and on the other it was endeavoured to understand the details of the mechanism of the elementary chemical reaction under the conditions of high energy.

In Eqn.(1) the probability of the reaction $p(E)$ can be represented by the relation

$$p(E)=\sigma_r(E)/[\sigma_r(E)+\sigma_n(E)],$$

where $\sigma_r(E)$ is the "reaction" collision cross-section, i.e. the cross-section of the collision leading to reaction, and $\sigma_n(E)$ is the cross-section of the "non-reaction" collision in which the "hot" atom loses energy without entering into a reaction with formation of a stable product. The main efforts were concentrated on the search for an analytical expression for $n(E,E')$. Thus Estrup and Wolfgang[161] used the ideas of the physics of the moderation of neutrons, from which it followed that, for neutral species generated with $E \gg E_2$ (E_2 is the "upper limit" to the occurrence of chemical reactions), the energy spectrum of the species can be described by the Fermi function

$$n(E, E')\,dE'=n(E')\,dE'=dE'/\alpha E',$$

where α is the average loss of energy determined as the retardation coefficient for two consecutive collisions: $E_{i+1}=E_iE^{-\alpha}$. An expression for α can be obtained by specifying the moderation mechanism. Since the form of the function $p(E)$ is not clear, the parameter

$$I=\int_0^\infty p(E)\,dE,$$

called the integral reaction probability, was introduced[162].

Using the concepts enumerated above, an expression was obtained for the yield of the reaction:

$$R=1-\exp\left(-\frac{f}{\alpha}I\right),$$

which is at present widely used in the chemistry of "hot" atoms (f is the geometrical probability of the collision calculated from the mole fractions of the substances and the covalent atomic radii). Subsequently the equation was supplemented by corrections for the influence of added substances and for the phenomenon of the "combustion" of the species in the course of the reaction[163]. The Wolfgang equation agrees satisfactorily with experiment, i.e. a relation of the type

$$-\ln(1-R)=\frac{f}{\alpha}I$$

persists when the ratio f/α is varied within wide limits.

The ratio f/α has been calculated from the experimental conditions and the efficiency of moderation. The quantity I has been determined graphically. The integral probabilities of many reactions of "hot" ^3H atoms have been found in this way. Thus $I=0.1$ for the reaction $^3H+CH_4 \rightarrow CH_3^3H+H$, i.e. approximately one of ten collisions leads to reaction[161]. The possibility of using the ideas of the physics of the moderation and reactions of neutrons for chemical reactions proved to be fruitful, because it was possible to replace the reaction cross-section by the integral probability and the moderation process by a simple collision model.

The Wolfgang equation holds better the higher the initial energy of the atoms and the smaller the influence of non-elastic collisions. In studies since 1969 α has been calculated on the basis of a retardation scheme for rigid spheres. Subsequently account was taken in the moderation model of the possibility of "soft" collisions and it was found that the reaction yield should increase for a "softer" potential[164]. After taking into account the scattering anisotropy, it was shown that α decreases under these conditions, but the form of the collision density function remains unaltered[165].

The models examined are valid for energy ranges remote from the energy of the source of "hot" atoms, i.e. $E \ll E_0$ (but $E_0 \gg E_2$)[166]. In the theory developed by Porter[167-169] these limitations were removed by solving the equation for the reaction probability as a function of energy; account was also taken of the thermal movement of the target species. Porter's equation for the yield of the reaction with formation of the ith product is

$$R_i(E)=p_i(E)+\left[1-\sum_j p_j(E)\right]\int_0^\infty R_i(E')\,W(E, E')\,dE', \qquad (5)$$

where $p_i(E)$ is the probability of the formation of the product in the first collision, $[1-\sum_j p_j(E)]$ the probability of avoiding reactions with formation of all the products, $W(E,E')$ the probability of a change in the energy of the atom ($E \rightarrow E'$) in a non-reactive collision, and $p_i(E')$ the probability of the reaction in the collision of reactants with $E=E'$. Porter derived Eqn.(5) by a rigorous mathematical procedure, although it can be formulated on the basis of the most general intuitive considerations. An analytical solution of this equation is possible on the assumption of a simple moderation model, namely collisions of the bard sphere type[170].

Thomsen[171] treated the reactions differently. His formulation of the problem differs by the fact that, instead of seeking a solution for the stationary distribution of "hot" atoms, he suggested that one determine the probability of the reaction for an individual atom in the course of its moderation. The moderation process was then modelled as a continuous process.

Theoretical studies have shown that the atomic spectrum depends greatly on the properties of the medium. It was concluded that the probabilities of the reactions of "hot" atoms with different substances should be compared by studying experimentally the yields of reactions in the presence of a moderating substance. Naturally the inert gases were chosen for this purpose. Different variants of stochastic methods began to be used for quantitative estimates. In particular, the collision densities at different temperatures of the gas medium have been calculated for ^3H atoms with "intermediate" energies (0.5–2 eV) and for three potentials (the solid sphere, Lennard–Jones, and $1/r^6$ potentials). It was shown that, for an energy of the source of 0.5 eV, oscillations in collision density are observed, which had been predicted theoretically for the moderation of neutrons[172], and for $E < 0.5$ eV a rapid approach to the collision density corresponding to the $1/E$ spectrum is observed. The influence of temperature is manifested by the fact that, in the energy distribution spectrum of the species, a "tail" appears in the high-energy region for $E > 0.5$ eV.[173]

Subsequently a stationary model of the moderation of "hot" species was proposed in which a Maxwell distribution of "hot" atoms with an average temperature $T_R(t)$, depending on the time elapsed from the instant of generation of the atoms, was assumed[174]. A stationary state obtains when $dT_R(t)/dt=0$. An analytical solution of the Boltzmann equation for the transport of the species is then possible, and the final expression is similar to the Arrhenius equation.

The condition for the attainment of a stationary state up to the instant when chemical reactions begin to occur to an appreciable extent is very important for the application of this model. However, it has been established by the Monte Carlo method that the stationary states do not obtain a retardation[175,176]. A study was therefore undertaken with the aim of a more accurate solution of the Boltzmann equation and a clear-cut framework has been found for the application of the proposed theory: the time scales in the description of the moderation processes and the reactions must be separated[177]. Conditions have been established under which the solution of the Boltzmann equation satisfies the calculations by the Monte Carlo method or agrees with the distribution of the species with respect to velocities corresponding to a Maxwell distribution at an effective temperature[178].

The transfer of the ideas of nuclear physics to moderation and the reactions of chemical species proved so productive that investigators were inspired to consider more far-reaching analogies between chemical and nuclear reactions. The description of resonance reactions involving neutrons is widely used in nuclear physics. The Breit–Wigner formula relates the reaction cross-section to the resonance parameters. It has been suggested that resonance scattering cross-sections and reactions involving a polyatomic molecule correspond to the resonance cross-section for the scattering of the "hot" atom by the attacked atom in the molecule and the case where the cross-sections for the reactive and non-reactive collisions of the "hot" atom with a molecule involve only one Breit–Wigner resonance was examined[37].

These qualitative ideas required a rigorous mathematical justification, which was subsequently provided[38]. The following expression has been obtained for the yield of the "hot" reaction:

$$R \propto \Gamma/\beta ,$$

where Γ is the width of the resonance, $\beta = \mu'/(\mu' + m)$ the "isotope" factor associated with the masses of the interacting atoms and characterising the degree of localisation of the "hot" reaction, μ' the mass of the part of the molecule involved in the formation of the resonance state, and m the mass of the "hot" atom. The authors[38] believe that the similarity of the mass μ' to the mass of the attacked atom (μ' was calculated from the isotope effect in the reactions involving the abstraction of hydrogen by "hot" tritium atoms) constitutes significant evidence for the occurrence of resonance in the reaction. The value of the proposed interpretation of the mechanism of "hot" reactions consists in the fact that, within the framework of the theory, one can find an explanation of the marked influence of the electronic structure of the molecules and of the difference between the bond energies on the yield of the reaction—a fact which is well known in the chemistry of "hot" species[179–181].

We shall consider the achievements of the theoretical studies in the chemistry of "hot" atoms in relation to two reactions, namely $H + H_2 \rightarrow H_2 + H$ and $H + CH_4 \rightarrow CH_3 + H_2$, and also substitution reactions of the type $^3H + CH_4 \rightarrow CH_3{}^3H + H$.

2. The $H + H_2 \rightarrow H_2 + H$ Reaction and Its Isotopic Variants

The ratio of the integral probabilities of the reactions of "hot" recoil atoms, i.e.

$$^3H + HD \begin{cases} \rightarrow H^3H + D \\ \rightarrow D^3H + H , \end{cases}$$

has been calculated[170] as $I_{H^3H}/I_{D^3H} = 0.62 \pm 0.06$; the corresponding value, calculated in another study[182] from the results of trajectory calculations, proved to be 0.7 ± 0.1.

For the reactions $^3H + H_2 \rightarrow H^3H + H$ and $^3H + D_2 \rightarrow D^3H + D$, experiment yielded $I_{H^3H}/I_{D^3H} = 1.14 \pm 0.06$, while the calculated value is 1.18 ± 0.05. Since a satisfactory agreement has been observed between the calculated and experimental data, it is reasonable to consider in greater detail the essential features of the calculations yielding valuable information about the details of the reaction mechanisms.

The potential surface for a reaction of the type $A + BC \rightarrow$ was constructed[182] on the basis of the Morse function taking into account the energy levels obtained in the solution of the secular equation and neglecting overlap (the Hückel method)[182]:

$$U = E_1 + E_2 + \sum_{ij} H_{ij};\ H_{ij} = -D_{ij} \exp\left[-\beta_{ij}(r_{ij} - r_{0ij})\right] ,$$

where D_{ij} is the dissociation energy, β_{ij} the Morse constant, and r_{0ij} the equilibrium distance. The usual procedure was used in the subsequent calculations. It was found that, for low energies of the ^3H atoms (approximately 10 eV), the reaction cross-sections are a maximum for attack along the H–H (H–D, D–D) bond. For energies of approximately 35 eV, the cross-section is a maximum when attack takes place at right-angles to the H–H bond. This collision, leading to the abstraction of an atom (the "stripping" mechanism), is related to the "spectator" model: the process takes place in such a way that one atom is assumed to be abstracted, while another behaves as a passive witness of the event. On further increase of E to approximately 100 eV, the cross-section shifts towards collision angles $>\pi/2$, which indicates back-scattering of the reaction product ("rebound stripping"). In this process the third atom is a partner in the removal of the excess energy transferred by the "hot" atom on collision. The product molecule, formed as a result of this process, has a lower energy than the molecule obtained via the "spectator" mechanism (for the same collision energy).

Detailed calculations for reactions of the type

$$^3H + HD \begin{cases} \rightarrow H^3H + D \\ \rightarrow D^3H + H \\ \rightarrow {}^3H + D + H \end{cases} \qquad (6)$$

have been made recently[170] by the trajectory method up to $E_H = 60$ eV and cross-sections [including the cross-section of reactions (6)] and the integral probabilities of reactions have been obtained taking into account the contribution of non-elastic collisions to the atom moderation spectrum. It was found that the calculated ratio $I_{H^3H}/I_{D^3H} = 0.7$ agrees fairly well with the results of calculations based on simpler mechanisms (collision of the solid sphere type) and with experiment only in the region of low energies (of the order of several eV). For ^3H atoms with $E = 60$ eV, the calculated ratio $I_{H^3H}/I_{D^3H} = 1.8$, which is greater than the experimental value (for "hot" recoil atoms) and the value calculated on the basis of a simpler model (0.8). According to the authors[170], the reason for this discrepancy consists in the fact that their model is based on the assumption of a small role of secondary dissociation reactions of the H^3H and ^3HD molecules. The agreement between the calculations based on the simple model and experiment is apparently attained as a result of the superposition of two errors—associated with the use of an incorrect function for the energy distribution of atoms (its calculation was based on the assumption of a moderation mechanism in accordance with the law governing hard sphere collisions) and the neglect of secondary dissociation.

Thus an exact description of the mechanism of even the simplest reactions is still not available, although there is no doubt that computational methods involving computers have thrown much light on it.

3. The Reaction $H + CH_4 \rightarrow H_2 + CH_3$ and Its Isotopic Variants

The abstraction reaction involving thermal hydrogen atoms is well known. For "hot" H*, D*, and ^3H* atoms, obtained by photolysis or via a nuclear reaction, channels other than the abstraction reaction

$$^3H + CH_4 \rightarrow CH_3 + H^3H, \quad (7)$$

have been discovered, namely

$$^3H + CH_4 \rightarrow CH_3{}^3H + H, \quad (8)$$

$$^3H + CH_4 \rightarrow CH_3 + H + {}^3H, \quad (9)$$
$$^3H + CH_4 \rightarrow CH_2{}^3H + 2H.$$

The calculation thresholds for the abstraction and substitution reactions, equal to 0.66 and 1.54 eV,[183] agree with experimental values of 0.3 and 1.5 eV.[8,184,185]. Experiments with $CH_4 + CD_4$ mixtures showed that $(H^3H/CH_4) : (H^3H/CD_4) = 1.4$, i.e. that CD_4 is somewhat less reactive in the abstraction reaction than CH_4. The ratio $(CH_3{}^3H/CH_4) : (CD_3{}^3H/CD_4) = 6.9$ shows that CD_4 is significantly less reactive in the substitution reaction than CH_4.[186]

In the first trajectory studies the CH_3 group was approximated by a structureless unit with a mass of 15 and the LEPS potential was adopted as the potential energy surface[187]. It was found that the abstraction and substitution reactions are of the "direct" and "concerted" type, i.e. they proceed without the formation of a long-lived complex: the length of the bond dissociated increases monotonically with the simultaneous formation of a new bond. This process is apparently valid for $E \cong 1.5$–2 eV. For a higher energy (~10–15 eV), abstraction again predominates, but the mechanism is in this instance different—this is a "stripping" reaction. Since the CH_3 group has been represented by a single species, the problem of the details of the mechanism (whether or not the Walden inversion occurs) was not discussed in the above investigation[187].

Certain theoretical evidence for the mechanism of the Walden inversion has been obtained by considering the movements of all the atoms in the reaction between H and CH_4 along an empirical potential surface (no account was then taken of the interaction between the displaced H atom and the other three hydrogen atoms)[188,189]. The threshold of the abstraction reaction has been estimated as 0.4 eV and the cross-section is a maximum ($3.5\ Å^2$) for 2.7 eV. The authors showed that the calculated ratio of the probabilities of reactions (8) and (7) is not 0.25, as was observed in the experiments. Since it was assumed in the calculations that there is no Walden inversion, the above discrepancy throws doubt on the validity of this assumption.

In subsequent studies this limitation in the interaction between atoms was abandoned and all the hydrogen atoms began to be regarded as equivalent. It was shown[190] that the substitution of hydrogen and deuterium in the reaction between ^3H and CH_2D_2 involving the Walden inversion must be equally probable, which agrees with experimental results[9,186]. However, the calculations were performed using data for the reactions of tritium atoms with CH_4 and CD_4, i.e. semiempirically. These studies were followed by a series of investigations by MO methods in terms of various approximations, which yielded contradictory information about the role of the Walden inversion in the reaction mechanism[191,192].

The most detailed study has been made by Raff[82], who calculated the minimum on the CH_5 potential energy surface and calculated the cross-sections by the method of trajectories. It was found that the threshold of the abstraction reaction corresponds to 0.25 eV, while that of the substitution reaction corresponds to 1.5–1.6 eV. The cross-section of the abstraction reaction is a maximum at 1.5 eV and that of the substitution reaction is a maximum at 6 eV. The fragmentation process (9) begins according to these calculations at $E \cong 5$ eV and reaches a maximum at 10 eV, its probability decreasing slowly up to 40 eV. In the substitution reactions there is not more than 50% inversion, i.e. the Walden inversion does not constitute the only reaction mechanism. This conclusion was reached after considering the ^3H–C–H angles in trajectory studies of substitution reactions. In order to compare the results of the calculations with the results of experiments carried out previously for recoil atoms, Raff used Porter's equation for a stationary target[167] in conjunction with his own data obtained from trajectory studies. The limit of the ratio $H^3H/CH_3{}^3H$ (for high values of E), equal to 0.79, proved to be in excellent agreement with Wolfgang's experimental data for recoil atoms[18]. The ratio $CD_3{}^3H/D^3H$ proved to be somewhat smaller than the experimental value. Agreement with experimental data has not been achieved for photolytic atoms ($E \cong 2.8$ eV): calculation yielded $H^3H/CH_3{}^3H = 8.7$, while the experimental value is ~4. This may be because the Walden inversion mechanism plays a major role for a low energy.

4. Abstraction Reactions and the Influence of the Bond Energy on Their Yield

In the chemistry of "hot" tritium atoms the influence on the abstraction reaction of a small change in the bond energy E_b of the abstracted atom is well known[9,180] and the cause of this phenomenon has been the subject of discussions[17,162,179–181,193]. According to one concept, the influence of the bond energy is seen when an intermediate collision complex is formed, while according to another this happens when the abstraction reaction proceeds via a "stripping" mechanism analogous to the familiar mechanism of nuclear reactions. The fact that the bond energy must influence the probability of the abstraction reaction when a collision complex is formed is so evident that it does not require elucidation. However, numerous data have shown that the reactions of "hot" atoms proceed via a "direct" mechanism. Therefore this explanation is not satisfactory.

The "stripping" mechanism explains the dependence of the abstraction cross-sections on the bond energy by the fact that the lower the value of E_b the greater the target distance over which an atom can be "stripped off", i.e. for the same reaction time the process can occur with a higher energy of the "hot" atom. Hence one may conclude that the excitation function for a chemical abstraction reaction $\sigma_{abs}(E)$ is determined over a wider energy range than the function for the substitution reaction $\sigma_{subs}(E)$, where the role of the bond energy is manifested to a much smaller extent. There is little information in the literature about the experimental measurement of the $\sigma_{abs}(E)$ and $\sigma_{subs}(E)$ relations over a wide energy range. Calculations by the method of trajectories using semiempirical potential energy surfaces have shown that the bond energy influences the cross-section for the abstraction reaction by altering the height of the barrier (confirmation of the Semenov–Polanyi rule). We may note yet another important factor, which follows from these calculations: for a lower barrier, the reaction takes place over longer target distances; for a high barrier (approximately

0.5 eV), the probability of the reaction diminishes with increase of the impact parameter and for a low barrier (approximately 0.2 eV) there is a probability maximum. Hence it follows that the conclusion concerning the dynamics of the abstraction reaction treated as a "stripping" process has been confirmed by trajectory calculations[179]

5. Substitution Reactions

Substitution reactions of the type $RX + H^* \rightarrow RH + X$ (X = H, etc), which are not observed in thermal chemistry, have aroused the greatest interest. It has been established that such a reaction results in the formation of vibrationally excited molecules, which decompose at low pressures. In the theoretical calculations of the yield of substitution reactions corrections are introduced for decomposition based on the ratio of the energy converted on collision into the internal energy of the molecules and the dissociation energy. The dependence on pressure and the concentration of other species is obtained experimentally and the contribution of the decomposition process is estimated. For the reactions of recoil tritium atoms with CH_3X (X = F, Cl, Br, or H), the observed yields of the product $CH_2{}^3HX$ were 58 ± 2, 40 ± 2, 33 ± 3, and 83 ± 3% respectively and the values corrected for decomposition (primary yields) were 64 ± 3, 75 ± 3, 78 ± 5, and 100 ± 5% relative to the yield of cyclo-$C_4H_9{}^3H$ formed from cyclo-C_4H_{10} used as a standard.

The results agree with the "impact" model[194]: the greater the radius of the shielding atom, the lower the yield of the hydrogen substitution reaction. However, conclusions corrected for decomposition indicate the opposite relation. Apparently the description of the substitution process adopted previously, in which account was taken only of the physical characteristics of the system—the masses of the atoms, their dimensions, the bond angles, and the angles of attack—is inadequate. More far-reaching driving forces were manifested in the substitution reaction, for example, the mutual influence of the atoms in the molecule on the reactivity of the "hot" atoms. The concept of the decisive influence of the electronegativity of the substituents on the hydrogen substitution process has been put forward[193]. The probability of the substitution of hydrogen depends on the electron density in the C–H bond: in CH_3F it is a minimum, which leads to the lowest yield of the substitution reaction. The yields of substitution reactions of the atoms X are 4.4, 7.1, 12.0. and 7.7%, which agrees with the changes in the C–X bond energy and not in the collision diameters, as was assumed previously on the basis of the collision model.

Certain details of the substitution processes become more understandable when isotope effects are investigated[9,186,190,193,195]. It has been found that the isotope effect in the substitution of H and D by ^3H is 1.30 ± 0.03 for different compounds. Initially this was attributed to differences between the retarding capacities of substances, which induce changes in the frequency of the collisions of "hot" atoms with molecules. However, for substances such as $(CH_3)_3CH$ and $(CH_3)_3CD$, $(CD_3)_3CH$, and $(CD_3)_3CD$, the isotope effects proved to be identical. Furthermore, the isotope effect in the substitution of fluorine in CH_3F and CD_3F is 1.4 ± 0.05.[196] Thus the isotope effect is manifested not only in the first stage of the process (the dislodgement of an atom), but also in the second stage involving the formation of a bond with the molecular residue. The formation of a bond in the substitution reaction obeys the "inertial" mechanism: the lighter the residue, the higher the rate of formation of a bond[194].

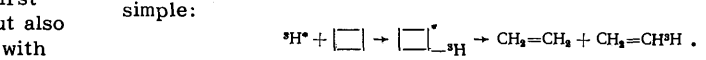
It would be very interesting to investigate the isotope effects in CH_2D_2: if the direct substitution process, i.e. the dislodgement of an atom, plays the main role, the isotope effect should be approximately 1.3, while in the case where the second stage (bond formation) is important, the yield of the substitution of deuterium should be approximately 10% higher by virtue of the "inertial" mechanism[17]. The technical difficulties in the separation of CH_2D^3H and CH^3HD_2 have now been overcome and it has been shown that their yields are identical, which demonstrates that both mechanisms operate, acting in opposite directions. The isotope effect for atoms with a lower energy is much greater: thus the ratio $(CH_3{}^3H/CH_4) : (CD_3{}^3H/CD_4)$ proved to be approximately 7 for ^3H atoms with $E = 2.8$ eV in the $CH_4 + CD_4$ mixture, the values for CH_3D and CH_2D_2 being 2.4 and 1.0. The overall yield of the substitution reaction falls with increase of the number of deuterium atoms in the molecule. The probability of the substitution reaction for an H atom is 1.6 ± 0.2 times greater than for a D atom regardless of whether the atom is substituted or remains in the residual radical, i.e. the two-stage mechanism of the substitution process has been confirmed[9].

The experimental threshold energy of the substitution of hydrogen in hydrocarbons by its isotopes is 1.5 eV.[184,186] For the substitution of hydrogen in 1-chlorobutane by ^3H atoms accelerated in a "chemical" accelerator, $E_{thresh} = 1.2$ eV has been obtained with a maximum reaction cross-section at 8 eV.[196] The threshold energy of the substitution of H by ^3H agrees with Eyring's theoretical estimate[197] for the substitution of H by D in CH_4, based on the assumption of an inversion mechanism. This was confirmed by certain subsequent investigations[190–191], but in others it was pointed out that a threshold energy of the substitution process of approximately 1.6 eV is obtained if the extent of inversion is not greater than 50%.[82] For bulky substituents in methane, the conservation of the initial configuration in substitution reactions has been demonstrated for a fairly large number of examples. This provided Wolfgang with justification to formulate, by analogy with the familiar Franck–Condon principle, the "golden rule of hot chemistry": "If the time required for the migration of atoms (with formation of a given reaction product) is greater than the collision time, the reaction is forbidden".[194]

One of the interesting features of the substitution reaction is the formation of excited molecules. The problem arises whether the energy is distributed among the degrees of freedom in such molecules before decomposition or before deactivation. Studies have shown that, as a result of the substitution of an H atom by a recoil ^3H atom, the molecules are vibrationally excited up to an energy of 5 eV, [16] and the hypothesis of a statistical distribution of energy proves to be valid. Indeed, according to the unimolecular decomposition theory[198], the probability of the decomposition is proportional to the energy excess over E_a:

$$k \simeq A[(E - E_a)/E]^{s-1},$$

where $s = \frac{1}{2}(3N-6)$ and N is the number of atoms in the molecule involved in the process. The probability of decomposition can be estimated from the yields of products and E_a is known from the "usual" chemistry. $E \cong 5$ eV have been calculated for the reactions of ^3H with cyclobutane[199] and methylcyclohexene[198]. In this case, the reaction mechanism is simple:



In a later study it was established that the reaction products can be obtained not only via unimolecular decomposition but also via a direct substitution reaction[200], i.e. after the substitution of H by ^3H the molecule can decompose until the

collision energy is uniformly distributed among all the vibrational degrees of freedom. This process can be described as a reaction involving the direct substitution of a group of atoms.

6. Addition Reactions

The reactions involving the addition of thermal hydrogen atoms to double bonds are accompanied by the liberation of a vibrational energy of approximately 30 kcal mol^{-1}. Some investigators have been interested in the possibility of obtaining superexcited radicals by the addition of "hot" atoms. In a series of studies[12,201], performed using photochemical atoms with $E = 1.8$ eV, the formation of such radicals was demonstrated by comparing the rate coefficients for the characteristic reactions of the radicals—the abstraction of hydrogen and recombination.

According to the Arrhenius equation, the probability of the reaction should approach the value of the steric factor as the interaction energy of the species increases. However, it has been shown in a number of investigations that the steric factors for the addition of hydrogen to ethylene increase by three orders of magnitude on passing from the thermal energy of hydrogen atoms, corresponding to room temperature, to 6 eV.[12] An analogous behaviour has been observed for the recoil tritium atoms in a cyclohexane-cyclohexene mixture[202]: the ratio of the rate coefficients for the abstraction and addition reactions was 0.34 ± 0.01, which exceeds by a factor of 100 the corresponding ratio for thermal atoms and by a factor of 5–20 the ratio of hydrogen atoms obtained in radiolysis under the influence of radiations of different types. The fraction of "hot" hydrogen atoms in the overall yield of hydrogen atoms in radiolysis (<15%) has been estimated from the data of Kukin and Filatov[202]. An analogous result had been obtained earlier for the CH_3OH–C_6H_6 mixture, where the corresponding ratio of the abstraction and addition rate constants was close to unity, while in radiolysis it was approximately 10^{-2}.[203] This agrees with quantitative estimates of the contribution of the reactions of "hot" atoms obtained in radiolysis to the yield of H_2.

Since the steric factor for an abstraction reaction involving thermal hydrogen atoms is 0.1–1 and that for an addition reaction is 10^{-3}–10^{-4}, it follows that k_{abs}/k_{add} should be 10^{-2}–10^{-4} for $E \gg E_a$. Since the experimental ratios of the rate coefficients for "hot" atoms are close to unity, the steric factors for the reactions apparently also depend on the energy.

7. Other Reactions of "Hot" Hydrogen Atoms

The reactions of "hot" hydrogen atoms not observed in the "usual" thermal chemistry have been noted in a number of studies: reactions involving the substitution of groups of atoms[9,17,162,204] and the dissociation of C–C bonds[205–207]. Certain polymerisation reactions with participation of "hot" tritium atoms have been studied[208,209]. These reactions, first noted for recoil tritium atoms, were subsequently investigated with the aid of the acceleration technique[10,210]. The energy thresholds of certain reactions, for example, the cyclohexane ring opening reaction (approximately 4.5 eV), have been found[210]. There are at present no clear ideas in the literature concerning the mechanisms of the above processes.

In the study of chemical processes from the standpoint of elementary reaction collision steps, the knowledge of the reaction cross-section is the most valuable. Classical experimental chemistry operates with the concept of the rate constant which is identical with the rate coefficient for the Maxwell–Boltzmann distribution of species. Information about the cross-section cannot be obtained from numerical rate constants, since the cross-section is a characteristic of the reaction for specific quantum states of the reactants and products.

The possibility of the calculation of the cross-sections and of estimating other reaction characteristics has been considered in detail in a review[211], where a table of the rate coefficients, the integral probabilities, and the cross-sections of the reactions of hydrogen atoms obtained by various procedures is compiled.

IV. CONCLUSIONS

Thermal hydrogen atoms exhibit a high reactivity up to approximately 30 K in relation to compounds of virtually all classes. The view that the reactions at low temperatures proceed via a tunnel mechanism is generally accepted, although it has been suggested that the deviation from the Arrhenius relation at low temperatures can be caused by a change in the activation energy in the solid state.

Significant advances in the understanding of the mechanisms of reactions involving hydrogen atoms have been made by virtue of the development of physical ideas about the reaction dynamics. The MO methods in combination with computer calculations are widely used. Calculations of the potential energy of the interaction of six bodies have now become possible, which greatly extends the applied scope of the calculations.

Apart from the familiar reaction channels, the following new channels have been established for "hot" hydrogen atoms: the substitution of atoms and groups of atoms. Since the products of the unimolecular decomposition of the initial molecules are present in the reactions of "hot" atoms, it is believed that substitution results in the formation of vibrationally excited molecules, the probability of the decomposition of which can be calculated. "Hot" atoms can add to the double bond with formation of vibrationally "superexcited" radicals. Concepts such as the reaction rate coefficient (and not the rate constant, since there is no Boltzmann distribution with respect to the energies), the reaction probability, and the reaction cross-section serve as quantitative characteristics of "hot" reactions. Their dependence on the collision energy is significant.

Studies with "hot" atoms stimulated the investigation of the dependence of reaction probability on the energy of the colliding species. A successful development of the relevant studies requires the theoretical knowledge of the form of the potential surfaces for the reactions. The dependence of the reaction cross-sections on the energy can be obtained by the method of trajectories. The conversion of the cross-sections into reaction probabilities and yields presents no difficulties. On the other hand, if account is taken of the orientation of the molecule relative to the velocity vector of the attacking species, it is possible to obtain the dependence of the differential reaction cross-section on the angle of attack. However, this is applicable only to a quantitative description of simple reactions. For more complex processes, there is a possibility of only a qualitative comparison with experiment. Nevertheless, computational methods have contributed much to the understanding of the dynamics of chemical reactions. Apparently Mulliken was right in predicting the onset of the era of "computing"chemists who will resort to computers in their hundreds and will achieve thereby a significant understanding of the reaction mechanisms.

Experimental studies with "hot" species require the construction of complex accelerators, because the traditional methods for the generation of species (photolysis, radiolysis, and nuclear reactions) cannot yield a stream of monochromatic atoms with a specified energy and the value of such experiments is therefore theoretically low. Information about the quantum states of the reactants and products is essential for a comparison of experimental data with theoretical calculations. This also requires a quantitatively new development of experimental techniques.

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Methods of Synthesis and Properties of β-Dimethylaminoethyl and Choline Esters of Aminoacids and Peptides

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The literature data on the synthesis of β-dimethylaminoethyl and choline esters of aminoacids and peptides are surveyed. The N-protecting groups used and methods for their removal as well as the physicochemical and biological properties of the above compounds are considered.
The bibliography includes 69 references.

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I. INTRODUCTION

The choline esters of aminoacids and peptides have a comparatively short history. Their structure resembles that of acetylcholine (AC), which has aroused much interest in recent years in their synthesis and biological activity. After a comparatively short time, research into both active cholinomimetics, isolated from plant and animal raw materials[1-4], and synthetic choline esters of aminoacids and peptides developed on a fairly wide scale. Studies have also been made[5-7] in which dialkylaminoalkyl esters were used as C-protecting groups for peptide synthesis.

This review deals with methods of synthesis of β-dimethylaminoethyl and choline esters of aminoacids and peptides and also with their physicochemical and biological properties. In the development of methods of synthesis of dialkylaminoalkyl aminoacid and peptide esters use is made of the fundamental postulates of peptide chemistry according to which the appropriate protecting groups, methods of synthesis of the ester, and methods for the removal of the protecting group and the isolation of the final product are selected.

II. PROTECTING GROUPS

In peptide synthesis one of the main tasks is the protection of the amino-group of the aminoacid or peptide. This problem remains just as acute in the synthesis of choline and β-dialkylaminoalkyl esters of aminoacids and peptides.

The majority of investigators[5,8-14] used the benzyloxycarbonyl (Z) group† as the *N*-protecting group in the synthesis of the esters, its removal after the synthesis of the aminoesters being achieved by treatment with hydrogen bromide in glacial acetic acid[5,8-13] and by catalytic hydrogenolysis over palladium[5]; these groups have been removed from the choline esters of certain Z-aminoacids with phosphonium tri-iodide[15] or by hydrogenolysis over PtO_2.[16-19] It has been noted[16] that this involves partial cleavage of the ester linkage.

†Apart from the standard abbreviations recommended by the IUPAC-IUB Commission on Biochemical Nomenclature, the following abbreviations have been adopted here: Aba = aminobenzoic acid; ε-Aca = ε-aminocaproic acid; γ-A-β-Hbu = γ-amino-β-hydroxybutyric acid; ω-Ava = ω-aminovaleric acid.

The t-butoxycarbonyl (Boc) group[6,9,10,12,20] has been removed from β-dimethylaminoethyl esters by passing dry gaseous hydrogen chloride through an ethereal solution of the β-dimethylaminoethyl ester of the Boc-aminoacid[6] and also by treatment with trifluoracetic acid[9,12]. The protecting group has been removed from the choline ester of Boc-ε-aminocaproic acid[20] with a dilute solution of hydrogen bromide in acetic acid (10 min, 20 °C) or with a 48% solution of hydrogen bromide (2 min, 0 °C) and a 0.1 *N* solution of hydrogen chloride in formic acid (10 min, 20 °C).

The triphenylmethyl [trityl (Trit)] group has also been used successfully in the synthesis of the choline ester of glutamic acid; it was removed by treatment with hydrogen chloride[21] or acetic acid[22,23].

The possibility of using toluene-*p*-sulphonyl [tosyl (Tos)] and phthalyl (Pht) protecting groups has also been investigated[11]. It has been established that hydrazinolysis or acid hydrolysis under various conditions for the Pht group and reduction with sodium in liquid ammonia for the Tos group lead to partial cleavage of the ester linkage. According to the data of Mndzhoyan and Agadzhanyan[11], these protecting groups are less favourable for the synthesis of dialkylaminoalkyl esters of aminoacids with a free amino-group, in contrast to the Z and Boc groups. In the synthesis of the hydrochlorides of the β-dimethylaminoethyl and choline esters of glycine, the *o*-nitrobenzenesulphenyl (Nbs) group was used as the *N*-protecting group[24] and was removed by treatment with hydrogen chloride.

The majority of investigators using the acid chloride method for the synthesis of β-dimethylaminoethyl or choline esters of aminoacids protected the amino-group by protonation[15,25,26]. The study of Freundenberg and Keller[27], who used the acid chlorides of α-azidoacids, is unique in this respect (see Section III, 1 below). After the synthesis of the choline esters, the azido-group was converted into an amino-group by reduction over Pd/C in the presence of hydrogen chloride.

The dansyl (Dns) group has been used[28] in the synthesis of choline esters of certain aminoacids. In the synthesis of choline esters of aminoacids and peptides Kanaoka and coworkers[8,9] protected other functional groups as well as the amino-group, namely the hydroxy-group of tyrosine was protected by benzylation, the guanidino-group of arginine was protected by nitration, and the β- and γ-carboxy-groups of aspartic and glutamic acid were protected by benzylation. The β-carboxy-group of aspartic acid was protected[9] by t-butylation. The benzyl group has been used[6] to protect

the imidazole ring of histidine and the hydroxy-group of serine.

Table 1 presents data, in relation to glycine, concerning the use and conditions for the removal of various *N*-protecting groups in the synthesis of β-dimethylaminoethyl and choline esters by various methods. Evidently the best *N*-protecting groups which can be used in the synthesis of aminoesters of aminoacids and peptides are the Z, Boc, and Nbs groups: when they are removed, the final product is obtained in high yields.

Table 1. Conditions for the elimination of *N*-protecting groups from the β-dimethylaminoethyl and choline esters of *N*-protected glycines R-Gly-OCH_2CH_2X.

Conditions for elimination of *N*-protecting group			References
X=NMe_2	X=NMe_3·Hal	yield, %	
Boc-group			
F_3C—COOH; t_{room}, 1 h	—	94.4	[12]
Z-group			
HBr/AcOH	—	100	[5]
H_2/Pd	—	—	[5]
34% HBr/AcOH soln; t_{room}, 2 h	—	64.9	[12]
sat. HBr/AcOH soln	—	90	[10]
28% HBr/AcOH soln; t_{room}, 40 min	—	65	[13]
	25% HBr/AcOH soln; t_{room}, 30-60 min	—	[8]
—	28% HBr/AcOH soln; t_{room}	73	[13]
Nbs-group			
Methanol solution of HCl	—	89.5	[24]
—	methanol solution of HCl	81.5	[24]
Pht group			
1 M N_2H_4 soln in methanol; refluxing for 1 h	—	*	[11]
N_2H_4 (1 : 1); 50°C, 1 h	—	*	[11]
N_2H_4 (1 : 2.2); refluxing for 1 h	—	0	[11]
5 *N* HCl soln; water bath, 4 h	—	*	[11]
5 *N* HCl soln; refluxing for 2 h		*	[11]
Tos group			
Na/NH_3			[11]

*Mixture of products of the cleavage of the ester linkage and of the *N*-protecting group in the β-dimethylaminoethyl ester of *N*-protected glycine.

III. METHODS OF SYNTHESIS

1. The Acid Chloride Method

The acid chloride method was used mainly in early studies on the synthesis of choline esters of aminoacids and peptides. The hydrochlorides of the choline esters of glycine[15,25], glycylglycine[15], and methionine[26] were obtained by the reaction of the hydrochloride of the aminoacid chloride or peptide with choline on heating. The acid chlorides of *N*-protected aminoacids were used in the synthesis of both β-dimethylaminoethyl esters[11,15,29] and β-halogenoethyl esters[15], which are the starting materials in the synthesis of choline esters of aminoacids. It has been shown that the acid chloride method and the mixed anhydride method using the methyl ester of chlorocarbonic acid are approximately equally effective for the synthesis of the dialkylaminoalkyl esters of Tos- and Pht-glycine[11].

α-Azidoacyl chlorides[27] have also been used as the starting compounds for the synthesis of the choline esters of four aminoacids (glycine, DL-alanine, DL-leucine, and DL-valine):

Scheme 1

$$N_3\text{—}\underset{\displaystyle R}{\underset{|}{CH}}\text{—}CO\text{—}Cl + HOCH_2CH_2NMe_2 \rightarrow N_3\text{—}\underset{\displaystyle R}{\underset{|}{CH}}\text{—}COOCH_2CH_2NMe_2 \xrightarrow{MeI}$$

$$\rightarrow N_3\text{—}\underset{\displaystyle R}{\underset{|}{CH}}\text{—}COOCH_2CH_2\overset{+}{N}Me_3\bar{I} \xrightarrow{AgCl} N_3\text{—}\underset{\displaystyle R}{\underset{|}{CH}}\text{—}COOCH_2CH_2\overset{+}{N}Me_3\bar{Cl} \xrightarrow{Pd/H_2}$$

$$\rightarrow HCl\cdot H_2N\text{—}\underset{\displaystyle R}{\underset{|}{CH}}\text{—}COOCH_2CH_2\overset{+}{N}Me_3\bar{Cl}\ .$$

2. The Mixed Anhydride Method

This method has been used by many investigators in the synthesis of β-dimethylaminoethyl esters of *N*-protected aminoacids and peptides[5,10-13,30]. Mixed anhydrides obtained from *N*-acylaminoacids and benzenesulphonyl chloride, tosyl chloride, or methyl chlorocarbonate have been employed for the synthesis. However, in the case of the reaction of Pht-glycine with methyl chlorocarbonate the yield of the β-dimethylaminoethyl ester was insignificant[11]. Best results were obtained using isobutyl chlorocarbonate[12], but one should note that in this case the method involving the azeotropic distillation of water from the mixture of β-dimethylaminoethanol, *N*-acylaminoacid, and xylene proved to be more effective[13] than the mixed anhydride method.

It follows from a comparison of data published in different communications concerning the application of condensing agents in the synthesis of the β-dimethylaminoethyl ester of *N*-benzyloxycarbonylglycine by the mixed anhydride method (Table 2) that the best results are obtained when ethyl and isobutyl chlorocarbonates are used.

Table 2. The influence of substituents on the reactivity of mixed anhydrides in the synthesis of the β-dimethylaminoethyl ester of *N*-benzyloxycarbonylglycine via the mechanism Z-Gly-O—R + $HOCH_2CH_2NMe_2$ → Z-Gly-$OCH_2CH_2NMe_2$.

R	Yield, %	Refs.
$C_6H_5SO_2$	13	[10]
n-$CH_3C_6H_4SO_2$	26	[10]
MeOOC	40	[10]
EtOOC	58	[5]
iso-BuOOC	61*	[12]

*According to Shamshin et al.[13], the yield is 23.8%.

It is noteworthy that the yield of the β-dimethylaminoethyl ester of Z-glycine, obtained using isobutyl chlorocarbonate, was only 23.8%.[13] However, in other studies[12,30], the β-dimethylaminoethyl esters of *N*-protected aminoacids and peptides were synthesised using this reagent in high yields, which also confirms the effectiveness of isobutyl chlorocarbonate in the synthesis of the above compounds.

Two versions of the synthesis of the β-dimethylaminoethyl ester of *N*-benzyloxycarbonylglycylglycine (I) by the mixed anhydride method were investigated[30]:

$$\left.\begin{array}{l} Z\text{—}Gly\text{—}OH + H\text{—}Gly\text{—}OCH_2CH_2NMe_2 \xrightarrow{a} \\ Z\text{—}Gly\text{—}Gly\text{—}OH + HOCH_2CH_2NMe_2 \xrightarrow{b} \end{array}\right\} \rightarrow Z\text{—}Gly\text{—}Gly\text{—}OCH_2CH_2NMe_2\ . \quad (I)$$

The results obtained[30] show that pathway *a* gives higher yields of compound (I).

3. The Carbodiimide Method

The carbodiimide method has been used in the synthesis of choline[8], β-halogenoethyl[20], and β-dimethylaminoethyl[10,12,24] esters of *N*-protected aminoacids and peptides[12,30]. *N,N'*-Dicyclohexylcarbodiimide (Dcc) has been largely used as the condensing agent.

Studies[10,12] in which the β-dimethylaminoethyl esters of Z-glycine and L-valylglycine as well as Boc-glycine were synthesised by both the mixed anhydride and carbodiimide methods have shown that the latter method is less effective.

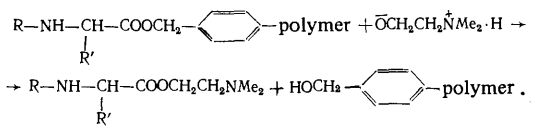
It has been reported[10] that the yield of the β-dimethylaminoethyl ester of Z-glycine obtained by the condensation of Z-glycine and β-dimethylaminoethanol with the aid of Dcc varies with the reactant ratio and reaction time. The authors[10] noted the formation of an appreciable amount (up to 50%) of *N*-benzyloxycarbonylglycyldicyclohexylurea as a side product. They also noted that at a reduced temperature the yield of the β-dimethylaminoethyl ester increases.

Subsequently the carbodiimide method was used successfully[8] in the condensation of certain *N*-acylaminoacids with choline. The carbodiimide method has been employed for the cross-linking of the methobromide of the β-dimethylaminoethyl ether of ε-aminocaproic acid with Sepharose 2B.[20]

4. The Activated Ester or Transesterification Method

p-Nitrophenyl esters of *N*-protected aminoacids have been largely used in the synthesis of β-dimethylaminoethyl choline esters by the activated ester method. The method has been applied in the synthesis of the choline ester of Z-glycine[24]. The β-dimethylaminoethyl esters of Z-L-leucylglycine and of the γ-methyl ester of L-glutamylglycine have been obtained by the reaction of the β-dimethylaminoethyl ester of glycine with the *p*-nitrophenyl esters of Z-L-leucine and of the γ-methyl ester of L-glutamic acid[5]. The cyanomethyl ester has been employed in the synthesis of the β-dimethylaminoethyl ester of *N*-benzoylsarcosine[31].

After synthesis by the solid phase method, the peptide linked to the polymer in the form of the benzyl ester has been subjected[6] to transesterification by treatment with β-dimethylaminoethanol at room temperature in accordance with the following scheme:



The influence of the solvent on the transesterification process has been tested in relation to Boc-glycine[6]. It was established that treatment with a 1:1 (by volume) mixture of β-dimethylaminoethanol and dimethylformamide (DMF) in the course of 70 h ensures virtually quantitative transesterification. When dioxan or methylene chloride was used, the degree of transesterification of the Boc-Gly-O-polymer with β-dimethylaminoethanol was much lower. The rate of transesterification in DMF has been studied in greater detail[6] in relation to the polymer-bound pentapeptide Boc-O-Bzl-L-Ser-L-Gln-NO_2-L-Arg-N^{im}-Bzl-L-His-Gly-O-polymer. It was established that the length of the peptide chain does not affect the rate of transesterification. The authors[6] also point out that the reaction is hindered in the case of valine and proline. It has also been found in relation to the transesterification of the compound Boc-L-Leu-L-Ala-O-polymer with β-dimethylaminoethanol that the degree of racemisation is insignificant (approximately 0.3 ± 0.1%).

The β-dimethylaminoethyl esters of Tos-glycine[31], hippuric acid, and hippurylglycine[32] have been obtained by the transesterification method involving the reaction of the methyl or ethyl esters of the *N*-protected aminoacids with β-dimethylaminoethanol in the presence of potassium cyanide as the catalyst.

5. Methods Involving the Azeotropic Distillation of Water

The possibilities of the synthesis of dialkylaminoalkyl esters of *N*-protected aminoacids by this method have been studied in detail in relation to the synthesis of the β-dimethylaminoethyl ester of Z-glycine[10,11] using different solvents and reaction times (Table 3). According to Mndzhoyan and Agadzhanyan[11], charring takes place in *o*-dichlorobenzene, while an increase of the duration of distillation of the azeotropic mixture in toluene results in an increase of the yield of the β-dimethylaminoethyl ester of Z-glycine. Subsequently this method was used successfully to synthesise the β-dimethylaminoethyl esters of Z-α- and ω-aminoacids[13].

Table 3. The influence of the solvent and reaction time on the yield of the β-dimethylaminoethyl ester of *N*-benzyloxycarbonylglycine in the azeotropic distillation of water.

Solvent	Time, h	Yield, %	Refs.
Toluene	23	25	[10]
Toluene	56	60	[11]
o-Xylene	23	50	[11]
o-Dichlorobenzene	23	20	[11]
Xylene	15—18	76 4	[13]

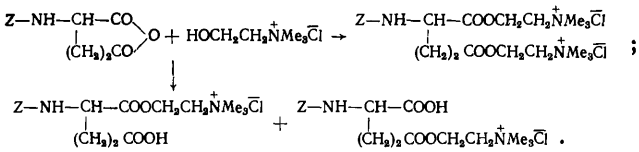
Comparison of the yields of the β-dimethylaminoethyl ester of *N*-benzyloxycarbonylglycine, synthesised by the method involving the azeotropic distillation of water from a mixture of the Z-aminoacid and the corresponding aminoalcohol in different solvents, makes it evident that xylene constitutes the best reaction medium.

6. Other Methods of Synthesis

One of the common methods of synthesis of β-dimethylaminoethyl esters of aminoacids and peptides involves the interaction of the *N*-protected aminoacids and peptides with dialkylaminoalkyl halides ($XCH_2CH_2NR_2$; X = Cl or Br) in the presence of bases such as triethylamine[8-10] or potassium carbonate[7,20,24]. The β-dimethylaminoethyl esters of di-, tri-, and tetra-peptides have been synthesised successfully by this method[9]. Good results have been obtained using potassium carbonate in the synthesis of the β-dimethylaminoethyl ester of Boc-ε-aminocaproic acid[20]. The β-dimethylaminoethyl ester of Nbs-glycine has been obtained analogously[24].

In a study of the degree of racemisation of the *C*-terminal aminoacid in the synthesis of choline esters, the authors[9] established in relation to Ac-L-Ile-$OCH_2CH_2\overset{+}{N}Me_3$.$Tos\bar{O}$ that the degree of racemisation does not exceed 1.2% for X = Br and 1.4% for X = Cl.

The interaction of one mole of the cyclic anhydride of Z-glutamic acid with two moles of choline yielded the corresponding dicholine ester[17,33]:



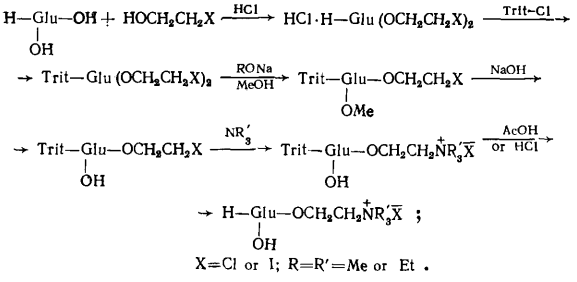
When equimolar amounts of the starting materials are used, a mixture of the α- and γ-choline ester is obtained[16,19,22].

Table 4. The β-dialkylaminoethyl and choline esters of *N*-protected aminoacids and peptides R-Am-$OCH_2CH_2NR'_2$.Y, where R′ = Me.

R	Am	Y	Yield, %	M.p.	Refs.
Boc	ε-Aca	—	100	liq.	[20]
Boc	*L*-Ala	—	65.0	liq.	[10]
Boc	Gly	—	60.2	liq.	[6, 12]
Boc	Gly-Gly	—	94.0	liq.	[6]
Boc	*L*-Leu-*L*-Ala	—	—	—	[6]
Boc	*L*-Ser(Bzl)-*L*-Gln-*L*-·Arg(NO_2)- *L* - His (Bzl)-Gly	—	85.0	liq.	[6]
Bz	Gly *	—	—	liq.	[7]
Z	γ-Abu	—	70.0	liq.	[13]
Z	ε-Aca	—	74.0	liq.	[13]
Z	*L*-Ala	—	78.0	liq.	[13, 30]
Z	β-Ala	—	70.0	liq.	[13]
Z	Gly	—	76.4	liq.	[8, 10—13]
Z	Gly **	—	50.0	65—67	[10, 11]
Z	*L*-Ile	—	57.2	liq.	[30]
Z	*L*-Leu	—	64.2	liq.	[30]
Z	*D*-Met	—	65.0	liq.	[30]
Z	*D*-Nval	—	83.0	liq.	[13]
Z	*D*-Phe	—	72.0	liq.	[30]
Z	*L*-Val	—	81.3	liq.	[13, 30]
Z	*m*-Aba-Gly	—	53.3	liq.	[30]
Z	*p*-Aba-Gly	—	58.6	liq.	[30]
Z	*L*-Ala-*L*-Phe	—	93.0	liq.	[6]
Z	*L*-Glu(OMe)-Gly	—	69.0	78—80	[5]
Z	Gly-Gly	—	62.2	liq.	[30]
Z	*L*-Leu-Gly	—	61.0	72—74	[5]
Z	*L*-Val-Gly	—	61.0	liq.	[12]
H	Gly	—	—	liq.	[12]
Nps	Gly	—	80.0	liq.	[24]
Pht	Gly	—	37.0	46—48	[11]
Pht	Gly *	—	30.0	88—90	[11]
Tos	Gly	—	42.0	55—57	[11]
Tos	Gly *	—	36.0	56	[11]
Ac	*L*-Ile	TosOMe	88.0	184—186	[9]
Boc	ε-Aca	MeI	86.0	94—95	[20]
Boc	*L*-Trp -*L*-Met-*L*-Asp(OBu-t-)-*L*-Phe	MeBr	72.0	114—116	[9]
Bz	Gly	MeBr	—	180—181	[31]
Bz	Gly	MeCl	25.0	91 (decomp.)	[32, 34]
Bz	Gly	MeCl·$AuCl_4$	—	173 (decomp.)	[34]
Bz	Gly	MeI	70.0	160—164	[32]
Bz	Gly	$Cr(NH_3)_2(SCN)_4Me$	—	135 (decomp.)	[34]
Bz	Gly *	MeBr	74.0	liq.	[7]
Bz	Sar	MeI	—	125—127	[31]
p-NO_2Bz	Gly	MeI	—	—	[31]
p-NO_2Bz	Gly	MeCl	64.0	189—192	[31]
	Gly-Gly	MeCl	81.3	222—225	[32]
Z	γ-Abu	MeI	50.0	123—125	[13]
Z	*L*-Ala	TosOMe	—	88—89	[8]
Z	*L*-Ala	H_2PtCl_6	34.0	195—197	[8]
Z	*L*-Arg(NO_2)	TosOMe	85.0	85—88	[8]
Z	*L*-Asp(OBzl)	TosOMe	—	131—133	[8]
Z	*L*-Asp(OBzl)	H_2PtCl_6	—	172—174	[8]
Z	*L*-$(Cys)_2$***	MeI	—	140—142	[15]
Z	*L*-$(Cys)_2$*	MeI	75.0	67—77	[15]
Z	*L*-Glu(OBzl)	H_2PtCl_6	—	154	[8]
Z	Glu ****	MeCl	90.6	—	[17—19, 41]
Z	Gly	HCl	—	110—112	[5, 7, 11, 12]
Z	Gly	H_2PtCl_6		156—161	[8]
Z	Gly	MeBr	80.0	113—114	[8, 13]
Z	Gly	MeI	68.7	195—198	[11, 13, 24]
Z	*L*-Ile	TosOMe	60.0	104—105	[8]
Z	*L*-Ile	H_2PtCl_6	—	149—150	[8]
Z	*L*-Leu	TosOMe	80.0	150	[8]
Z	*L*-Leu	H_2PtCl_6	—	190—192	[8]
Z	*L*-Lys	H_2PtCl_6	80.0	126—128	[8]
Z	*L*-Met	TosOMe	70.0	119—121	[8]
Z	*L*-Met	H_2PtCl_6	—	126, 128	[8]
Z	*D*-Nval	MeI	41.2	95—97	[13]
Z	*L*-Phe	MeBr	68.0	117—119	[8]
Z	*L*-Phe	MeI	—	59—62	[15]
Z	*L*-Phe	TosOMe	80.0	184—187	[8]
Z	*L*-Pro	TosOMe	65.0	81	[8]
Z	*L*-Pro	H_2PtCl_6	—	192—194	[8]
Z	*L*-Trp	TosOMe	35.5	83—85	[8]
Z	*L*-Trp	H_2PtCl_6	—	121—124	[8]
Z	*L*-Tyr(Bzl)	MeBr	60.0	58—61	[8]
Z	*L*-Tyr(Bzl)	H_2PtCl_6	80.0	148—150	[8]
Z	*L*-Val	MeBr	70.0	116—117	[8]
Z	*L*-Val	H_2PtCl_6	80.0	158—162	[8]
Z	*L*-Asp(OBu-t-)-*L*-Phe	MeBr	75.0	81	[9]
Z	*L*-Asp-*L*-Phe	MeBr	87.0	84—85	[9]
Z	*L*-Met-*L*-Asp(OBu)-*L*-Phe	MeBr	77.0	74—76	[9]
Z	*L*-Met-*L*-Asp-*L*-Phe	MeBr	84.0	85—87	[9]
Z	*L*-Trp-*L*-Met-*L*-Asp (OBu- t- *L*-Phe)	MeBr	73.0	89—91	[9]
Z	*L*-Trp-*L*-Met-*L*-Asp-*L*-Phe	MeBr	82.0	118—120	[9]
Z	*L*-Val-Gly	HCl	86.5	102—102	[12]
Dns	γ-Abu	MeBr	—	—	[28]
Dns	ω-Ava	MeBr	—	—	[28]
Dns	ε-Aca	MeBr	—	—	[28]
Dns	β-Ala	MeBr	—	—	[28]
Dns	Gly	MeBr	—	—	[28]
H	Gly	MeI	50.3	120—130	[12]
Nps	Gly	MeI	79.2	191—192	[24]
Pht	Gly	HCl	70.0	184—185	[11]
Pht	Gly	MeI	23.0	226—229	[11]
Pht	Gly	EtI	26.01	162—174	[11]
Tos	Gly	HCl	60.0	176—178	[11]
Tos	Gly	MeI	74.0	156—159	[11, 31]
Tos	Sar	MeI	86.0	142—144	[31]
Trit	*L*-Glu	MeI	54.0	—	[21—23]
Trit	*L*-Glu	MeCl	75.0	203	[33]

*R′ = Et.
**M.p. 35–36 °C.
***Dicholine ester.
****Monocholine ester.

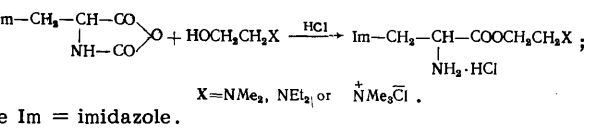
Another method of synthesis of the α-choline ester of glutamic acid has also been developed[21—33]:



Choline esters of hippuric acid[34] and certain Dns-aminoacids[28] have been synthesised analogously via β-halogenoethyl esters.

The synthesis of the hydrochlorides of the choline esters of γ-aminobutyric and β-hydroxy-γ-aminobutyric acids by the reaction of the corresponding acid and choline in the presence of gaseous hydrogen chloride in anhydrous dioxan has been described[35—37]. Choline esters of aminoacids can be obtained via their ammonium salts[26,33].

N-Carboxyanhydrides have been used[38] to synthesise the choline ester of L-histidine:



Here Im = imidazole.

Tables 4 and 5 present data on the synthesis of β-dialkylaminoethyl and choline esters of aminoacids and peptides.

Table 5. The hydrohalides of β-dialkylaminoalkyl and choline esters of aminoacids and peptides $HX.H\text{-}Am\text{-}OCH_2.CH_2NR'_2.Y$, where R′ = Me.

X	Am	Y	Yield, %	M.p.	References
Br	γ-Abu	HBr	82.0	173,5—175	[13]
Br	γ-Abu	MeBr	65.0	158—160	[13]
Cl	γ-Abu	MeCl	—	193—194	[1, 35, 36]
Cl	γ-Abu	$MeCl\cdot PtCl_4$	—	153—154 (decomp.)	[36]
Cl	γ-A-β-Hbu	MeCl	—	160 (decomp.)	[37]
Br	ε-Aca	HBr	72.0	169—172	[13]
Br	ε-Aca	MeBr	93.0	128	[13, 20]
Cl	ε-Aca	MeCl	75.0	—	[20]
Br	*L*-Ala	HBr	82.0	185—190	[10, 13, 30]
Br	*L*-Ala	MeBr	17.3	213—216	[8, 13]
Cl	*DL*-Ala	$MeCl\cdot PtCl_4$	—	237—239	[27]
Cl	*DL*-Ala	$MeCl\cdot 2AuCl_3$	—	—	[27]
Br	β-Ala	MeBr	33.3	185—187	[13]
F	*L*-Arg	MeF	—	56—57	[8]
Br	*L*-Asp	$MeBr\cdot H_2PtCl_6$	—	138—140	[8]
I	*L*-$(Cys)_2$*	MeI	—	83—95	[15]
Br	Glu **	$MeBr\cdot H_2PtCl_6$	—	185—188	[8]
Cl	Glu *	MeCl	60	146	[33, 41]
CH_3COO	*L*-Glu **	MeI	77	170—180	[17, 19, 21—23]
Cl	*L*-Glu **	MeCl	—	—	[18]
Br	Gly	HBr	100	186—187	[5, 10, 12, 13]
Br	Gly	MeBr	73.0	257—259	[8, 13]
Cl	Gly	MeCl	—	241	[15, 20]
Cl	Gly	$MeCl\cdot PtCl_4$	—	236—238	[25, 27]
Cl	Gly	$MeCl\cdot 3AuCl_3$	—	180—181 (decomp.)	[25]
Cl	Gly	$MeCl\cdot 2HgCl_2$	—	150—156 (decomp.)	[25]
$C_{14}H_7O_7S$	Gly ***	$C_{14}H_7O_7S$	—	259—260	[15]
$2C_6H_3O_7N_3$	*L*-His	$C_6H_3O_7N_3$	—	125—128	[38]
$2C_6H_3O_7N_3\cdot$	*L*-His ***	$C_6H_3O_7N_3$	—	142—145	[38]
Cl	*L*-His	MeCl	88.0	230 (decomp.)	[38]
Br	*L*-Ile	HBr	55.7	liq.	[30]
Br	*L*-Ile	MeBr	—	223—225	[8]
Br	*L*-Leu	HBr	53.6	liq.	[30]
Br	*L*-Leu	MeBr	—	188—190	[8]
Cl	*DL*-Leu	$MeCl\cdot PtCl_4$	—	203	[27]
Cl	*DL*-Leu	$MeCl\cdot 2AuCl_3$	—	—	[27]
Br	*L*-Lys	MeBr	—	63—65	[8]
Br	*L*-Met	$MeBr\cdot H_2PtCl_6$	—	138—140	[8]
Cl	*L*-Met	MeCl	—	151	[26]
Cl	*L*-Met	$MeCl\cdot PtCl_4$	—	195—197	[26]
Cl	*DL*-Met	MeCl	—	180	[26]
Br	*D*-Nval	MeBr	66.0	120—123	[13]
Br	*D*-Phe	HBr	61.6	—	[30]
Cl	Phe	MeCl	—	—	[15]
I	Phe	MeI	—	80—83	[15]
Br	*L*-Phe	MeBr	—	172—176	[8]
Br	*L*-Pro	MeBr	—	169—171	[8]
Br	*L*-Trp	MeBr	—	98—101	[8]
Br	*L*-Tyr	MeBr	—	68—72	[8]
Br	*L*-Val	HBr	57.6	—	[30]
Br	*L*-Val	MeBr	20.0	229—232	[8, 13]
Cl	*DL*-Val	$MeCl\cdot PtCl_4$	—	205—208	[27]
Cl	*DL*-Val	$MeCl\cdot 2AuCl_3$	—	217—218	[27]
Br	*m*-Aba-Gly	HBr	50.3	liq.	[30]
Br	*p*-Aba-Gly	HBr	51.3	liq.	[30]
Br	*L*-Asp-*L*-Phe	MeBr	75.0	126—127	[9]
Br	Gly-Gly	HBr	62.1	liq.	[30]
Cl	Gly-Gly	MeCl	—	128—130	[15]
Br	*L*-Met-*L*-Asp-*L*-Phe	MeBr	75.0	144—146	[9]
Br	*L*-Trp-*L*-Met-*L*-Asp-*L*-Phe	MeBr	77.0	126—128	[9]
Br	*L*-Val-Gly	HBr	93.6	liq.	[12]

*Dicholine ester.
**Monocholine ester.
***R′ = Et.

IV. PHYSICOCHEMICAL PROPERTIES

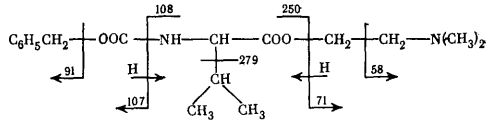
1. Physical Properties

The β-dimethylaminoethyl esters of Z- and Boc-aminoacids and peptides are mainly oily substances. Their hydrochlorides and hydrobromides are crystalline substances. The hydrohalides of choline esters of aminoacids and the dihydrohalides of dialkylaminoalkyl esters of aminoacids are as a rule crystalline; however, we should note that some of them are very hygroscopic. The choline esters of *N*-protected aminoacids and peptides are also crystalline.

Infrared spectroscopy has been widely used to identify β-dimethylaminoethyl esters of *N*-protected and unprotected aminoacids and peptides. The infrared absorption spectra of the β-dimethylaminoethyl esters of acylaminoacids have been investigated in detail[12,13] and it has been observed that characteristic peaks occur in the ranges 1680—1760 and 1625—1725 cm^{-1} and refer to the amide and ester carbonyl groups respectively. The presence of the ester bond in the β-dimethylaminoethyl esters of aminoacids and peptides independently of the *N*-protecting group has been confirmed[12, 30] by observing an absorption peak at 1265 cm^{-1}.

NMR has also been used to identify β-dimethylaminoethyl and choline esters of aminoacids and their derivatives[6,8,13,20,28].

A mass-spectrometric study of the β-dimethylaminoethyl esters of Z-α- and Z-ω-aminoacids[13] showed that the molecular ion peaks for these compounds have a low intensity or in many instances are not observed at all. This phenomenon has been explained[13] in relation to the β-dimethylaminoethyl ester of Z-valine by the ease of its decomposition with formation of stable radicals of the type $CH_2{=}N(CH_3)_2^+$ (*m/e* 58), $CH_2{=}CH{-}N(CH_3)_2^+$ (*m/e* 71), $C_6H_5CH_2^+$ (*m/e* 91), and $C_6H_5CH_2O^+$ (*m/e* 108):



The β-dimethylaminoethyl esters of p-alkoxybenzoylglycylglycines have also been studied by mass spectrometry[39].

Thin-layer and paper chromatography constitute some of the widely used physical methods for the identification of the β-dimethylaminoethyl and choline esters of aminoacids and peptides[5,6,8,9,11—13,16,20,26,30,33,34,38].

2. Chemical Properties

A study of the hydrolysis of the β-dimethylaminoethyl ester of Z-glycine by a 2—4% solution of sodium bicarbonate[5] established that the complete cleavage of the ester linkage takes place in the course of 40—70 min at room temperature. The β-dimethylaminoethyl ester of Boc-glycine in DMF has been hydrolysed[6] in the presence of water. It was observed that the time of complete hydrolysis of the ester diminishes with increase of the amount of water; in the presence of imidazole (0.1 equiv.), the rate of hydrolysis increases.

The ester group hydrolyses on refluxing an acid solution of the β-dimethylaminoethyl ester of Pht-glycine and also on removal of the Tos group by treatment with sodium in liquid ammonia[11].

It has been found that the spontaneous hydrolysis of hippurylcholine in distilled water proceeds at the same rate as the hydrolysis of acetylcholine[34]. The hydrolysis of the choline esters of Tos-glycine[31], hippuric acid[31,32], and hippurylglycine[32] has been investigated. γ-Aminobutyrylcholine (GABC) is unstable at pH 5.5, and is almost completely hydrolysed by 1 *N* HCL at 100 °C in the course of 30 min.[40]

The hydrazinolysis of the γ-choline ester of glutamic acid yielded the corresponding hydrazide[41]. The aminoacid hydrazide is obtained when the Pht group is removed from the aminoester of *N*-phthalylglycine[11].

The aminolysis of the ester linkage in the choline esters of the aminoacids has been investigated. Treatment of the α- or γ-choline esters of *N*-protected glutamic acid with a methanol solution of ammonia[41] yielded the corresponding amides.

In the search for activated esters suitable for the synthesis of peptides, a study has been made[7] of the possibility of using the choline esters. The reaction of the methobromide of the β-dimethylaminoethyl ester of hippuric acid with benzyl-amine gave rise to the expected benzylamide of hippuric acid in a yield up to 34%.

V. BIOLOGICAL PROPERTIES

The biological properties of the choline esters of aminoacids and peptides have been investigated fairly widely. Frank and coworkers synthesised diazoacetylcholine[42-44] and ε-aminocaproylcholine[20,45] in order to isolate acetylcholinesterase (ACE) and other enzymes specific to acetylcholine from the electric organs of the *electrophorus electricus*. It was established that ε-aminocaproylcholine is a full cholinergic (nicotinic) agonist. Its activity varies between those of acetylcholine and carbocholine; it is not hydrolysed by ACE and is not its inhibitor, but bound to Sepharose 2B it is an effective agent for the isolation of acetylcholine-binding receptors. The choline ester of *N*-dansyl-ε-aminocaproic acid was synthesised for the same purpose[28,46].

The biological action of GABC has been studied in detail. According to the results[1], GABC in a dose of 5×10^{-2} M suppresses the contracting action of acetylcholine, in a dose of 5×10^{-3} M it suppresses the action of histamine, and in a dose of 1×10^{-4} M it suppresses the secretion of gastrin. Eserine enhances and *d*-tubocurarine and flaxedil weaken the inhibiting influence of GABC on the transmission of neuromuscular impulses[47]. At a concentration of 5×10^{-4} g ml^{-1}, GABC induces the contractions of the small intestine in the guinea-pig and rabbit[48], which are not suppressed by atropine, hexamethonium, phenazoline, or a high concentration of serotonin; morphine appreciably weakens the antiserotonin effect of GABC.

Apart from its inhibiting effect on respiration, GABC also influences the cardiovascular system. GABC and glycylcholine reduce the tonus and the [contraction] amplitude of the isolated heart of the molusc *Mepetrix lusoria*[49]. According to Asano et al.[49], the inhibiting effect of GABC is due to its anticholinergic activity. The neurotropic activity of GABC [50] and its influence on the electric activity of the brain cortex[51] and the central nervous system[52,53] have been investigated. It has been established that GABC reduces the blood supply to the brain[54] but increases the permeability of the membranes[55].

The anticonvulsant properties of GABC [56] have been studied on mice, rabbits, and dogs. Glutamylcholine and GABC have an inhibiting effect on the primary sensory potential when the contralateral peraneal nerve is stimulated[57]. According to Takahashi et al.[57], the absence of an effect by intravenously administered glutamylcholine and GABC on the discharges induced by a solution of corazole is associated with the decomposition of these substances in the blood. It has been shown[40] that GABC is not hydrolysed by the ACE of the blood erythrocytes or the enzyme from the electrical organ of the eel, but is partly susceptible to the action of butyryl cholinesterase of the plasma and tissues, not being, however, a physiological substrate of this enzyme. The enzymatic hydrolysis of GABC [40] is inhibited by inhibitors of cholinesterase—eserine and di-isopropyl phosphorofluoridate. In the presence of α-oxoglutaric acid the action of the guinea-pig brain transaminase on GABC is not accompanied by transamination[40]. It has been established[13] that the choline esters of α- and ω-aminoacids exhibit a weak anticonvulsant activity; some of them possess hypothermic properties.

The results of tests on the influence of the hydrobromides of the choline esters of α-aminoacids on the contraction of smooth muscles[8] have demonstrated a cholinomimetic activity intermediate between those of acetylcholine and choline. It has also been established that the choline esters of cysteine and cystine exhibit an oxytocin activity[15]. Hippurylcholine suppresses the activity of blood serum cholinesterase by 90%.[34]

The choline ester of Nbs-glycine possesses a cholinomimetic activity[24] and also exhibits a pronounced antibacterial activity *in vitro* against *Staphylococcus aureus*. The dihydrochloride of the choline ester of L-histidine in a dose of 2 mg litre^{-1} intensifies the contraction of the isolated rabbit intestine and, when the dose is increased (to 5, 10, and 20 mg litre^{-1}), its contraction is inhibited. The picrates of β-dimethyl- and β-diethyl-aminoethyl esters of L-histidine enhance the contraction of the rabbit intestine in doses of 1 and 5 mg litre^{-1} respectively[38]. The methiodides of the β-dimethylaminoethyl esters of certain aminoacids and peptides are inferior in their cholinomimetic activity to carbocholine, but are much less toxic than the latter[58].

The mutagenic activity of the hydrochlorides of the β-dimethylaminoethyl esters of *p*-alkoxybenzoylglycylglycines has also been studied[59]. It has been established that some of them exhibit a pronounced mutagenic activity and that the latter depends on the structure of the alkyl moiety of the alkoxy-group.

The hydrolysis of the choline esters of certain *N*-protected aminoacids by chymotrypsin has been investigated[32,60]. A detailed study has been made of the hydrolysis of the choline esters of *N*-substituted aminoacids by ACE and butyrylcholinesterase[61] and also of their influence on the hydrolysis of acetylcholine. The dimethiodide of the β-dimethylaminoethyl ester of *N,N*-dimethylaminopropionic acid has been used as a model compound in the study of the hydrolysis of the dicholine esters of dicarboxylic acids by butyrylcholinesterase[62]. It has been shown that Z-glutamylcholine increases the activity of transmethylase and choline oxidase, prevents the decrease in the amount of phospholipids, and prevents the accumulation of fats in the liver[63-69].

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The Structure and Properties of Organocyclodisilazanes

Yu.M.Varezhkin, D.Ya.Zhinkin (deceased), and M.M.Morgunova

A survey and a systematic account of data on monomeric, oligomeric, and polymeric four-membered cyclic silazane systems are given and the fundamentals of the theory of their structure and reactivity are described. The physical and chemical properties, the methods of analysis, and certain aspects of the practical applications of these compounds are examined in detail. The review contains an exhaustive bibliography on organocyclodisilazane compounds starting from the first available information about them and extending up to 1978 (polycyclic systems in which the four-membered rings are linked via a silicon spiro-atom are excluded).
The bibliography includes 164 references.

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I. INTRODUCTION

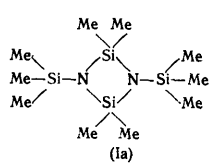
Continued progress in the modern chemistry of silicon- and nitrogen-containing compounds has led to the establishment and development of specific fields in this branch of chemistry such as the chemistry of four-membered cyclic silazane heterocycles—organocyclodisilazanes. This is associated both with the applied importance of compounds of this type, since they exhibit a high thermal stability, and with the interest in purely theoretical questions due to the somewhat unusual structure of these compounds.

A vigorous development of research not only into the synthesis of organocyclodisilazanes but also into the properties and structures of compounds of this class has taken place in recent years. In the study of these compounds almost the entire range of modern chemical methods has been used, including infrared Raman spectroscopy, ^{1}H NMR, mass spectrometry, and X-ray diffraction. Interesting data have been obtained but hitherto no attempts have been made to compile and survey all this information apart from a review published four years ago[1]. This review, which is devoted to the synthesis and applications of organocyclodisilazanes, covers a fairly wide range of problems and it is quite natural that many data concerning the structure and properties of these compounds have been omitted; furthermore, during the period which has elapsed since its publication, important new data have been obtained.

This review gives a systematic account and surveys the results of studies on the structures, properties, and reactivities of organocyclodisilazanes, and the possibilities of their practical applications are considered. Problems associated with the synthesis of monomers with the cyclodisilazane structure have already been described in detail[1-3].

II. THE STRUCTURE OF ORGANOCYCLODISILAZANES

Crystals of 1,3-Bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (Ia)

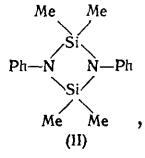


(Ia)

are monoclinic: $a = 6.75(2)$ Å, $b = 13.18(4)$ Å, $c = 11.22(3)$ Å, $\beta = 104°23' \pm 30'$, $V = 968.7$ Å^3, $D_m = 0.998$ (density determined by flotation in a diethylene glycol–methanol mixture), $Z = 2$, $D_c = 1.003$ (calculated density), space group $P2_1/n$ ($C_{2h}5$, No.14).[4]

Fig.1 shows that the silicon–nitrogen bonds in the cyclodisilazane ring are somewhat longer than exocyclic silicon–nitrogen bonds but shorter than the Si–N bonds in hexamethylcyclotrisilazane [1.78(3) Å].[5,6] The average length of the silicon–carbon bond (1.876 Å) corresponds to the usual values[7]. The distance between the opposite silicon atoms in the ring (2.476 Å) is somewhat greater than between the opposite nitrogen atoms (2.402 Å). The cyclodisilazane ring is highly strained compared with the hexamethylcyclotrisilazane (117° ± 4°) or octamethylcyclotetrasilazane (123° ± 4°) ring.[5,6] Compound (Ia) has a planar structure, which has been confirmed by ^{1}H NMR,[8] with the aid of which the unusually pronounced π-character of the exocyclic Si–N bond was observed in addition[9].

For 1,3-diphenyl-2,2,4,4-tetramethylcyclodisilazane (II)



(II)

the following parameters have been found: $a = 8.545(2)$ Å, $b = 16.820(3)$ Å, and $c = 11.622(2)$ Å; $V = 1670.38$ Å^3, $Z = 4$, $D_x = 1.187$, space group $Pbca$ (No.61).[10]

The molecule of compound (II) has a centre of symmetry; the cyclodisilazane ring is planar and the two benzene rings are parallel to one another. The length of the endocyclic Si–N bonds in compound (II) (see Fig.2) is greater than in compound (Ia); the length of the Si–N bonds is 1.728 Å in octamethylcyclotetrasilazane[11] and 1.732(2) Å in trisilylamine[12]. The distance between the opposite silicon atoms in the ring of compound (II) is 2.56 Å, which is somewhat greater than in compound (Ia), while the distance between the opposite nitrogen atoms (2.37 Å) is somewhat smaller.

The π-electron bond orders in compound (II) have been calculated by the Pariser–Parr–Pople (PPP) method: p(Si–N) = 0.346 and p(C–N) = 0.325. The latter agrees with the calculated value p(C–N) = 0.342, obtained[13] from

a modified Coulson formula. The results indicate a considerable contribution of the d_π–p_π interaction in the Si–N bond[10].

The structure of 1-methyldiphenylsilyl-3-(1,1,3-trimethyl-3,3-diphenylsilazanyl)-2,2,4,4-tetramethylcyclodisilazane (III) has been determined by X-ray diffraction[14,15]. The compound consists of colourless transparent monoclinic crystals: a = 15.790(10) Å, b = 8.443(5) Å, and c = 27.944(16) Å; β = 103.9(2)°, V = 3616.3 Å^3, D_m = 1.122 (determined by flotation), Z = 4, D_c = 1.124, space group $P2_1/c$ ($C_{2h}5$, No.14).[14]

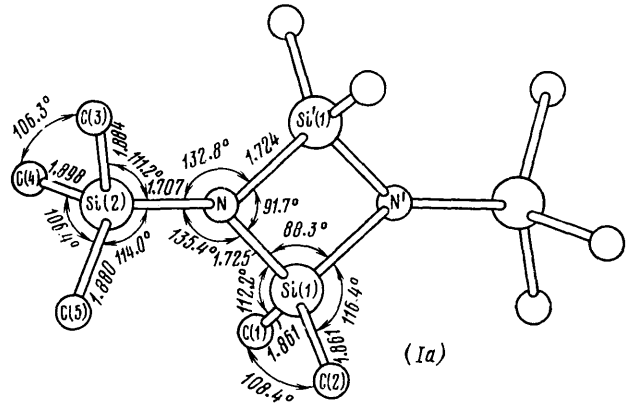


Figure 1. The bond lengths and angles in the 1,3-bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (Ia) molecule[4].

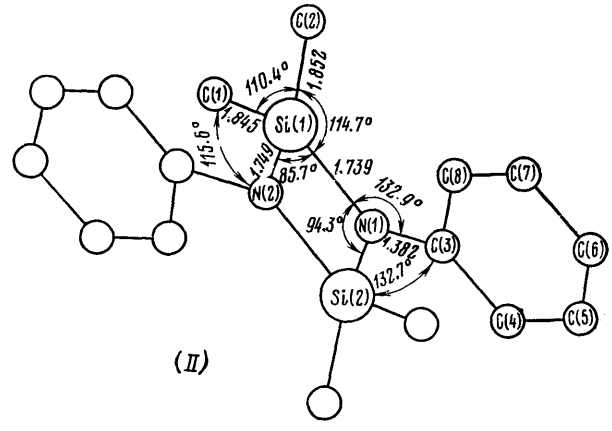


Figure 2. The bond lengths and angles in the 1,3-diphenyl-2,2,4,4-tetramethylcyclodisilazane (II) molecule[10].

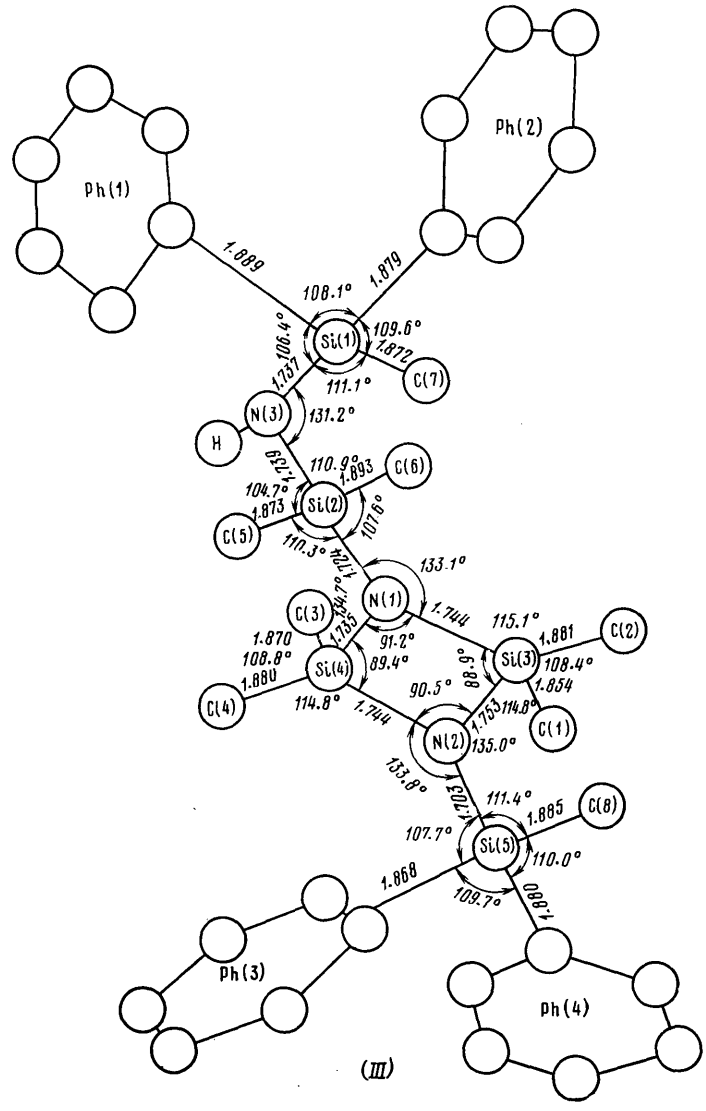


Figure 3. The bond lengths and angles in the 1-methyldiphenylsilyl-3-(1,1,3-trimethyl-3,3-diphenylsilazanyl)-2,2,4,4-tetramethylcyclodisilazane (III) molecule[14].

In compound (III) the average length of the Si–C(Me) bonds is the same as in compound (Ia) and corresponds to the usual value of 1.870 Å;[7] on the other hand, the Si–C(Ph) (1.879 Å) bond length is somewhat greater than the value usually adopted (1.843 Å).[7] The Si–N bonds in the ring are longer than the exocyclic bonds and than the Si–N bonds in the side chain (Fig.3). The distance between the opposite silicon atoms in the ring (2.484 Å) is greater, as in compound (Ia), than the distance between the opposite nitrogen atoms (2.448 Å). The torsional angles along the chain are Si(1)N(3)Si(2)N(1) = 80.19° and N(3)Si(2)N(1)Si(3) = 135.76°.[14]

The study of the crystal and molecular structures of 1,3-bis-(2,2,4,4,6-pentamethylcyclotrisiloxanyloxydimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (IV) showed[16] that the colourless crystals of this compound are triclinic, belong to the space group $P1$, and have the following parameters: a = 8.316(5) Å, b = 10.528(5) Å, and c = 12.320(4) Å; α = 76.65(3)°, β = 77.55(4)°, γ = 71.95(4)°, and Z = 1. The structure has been elucidated by a direct method and

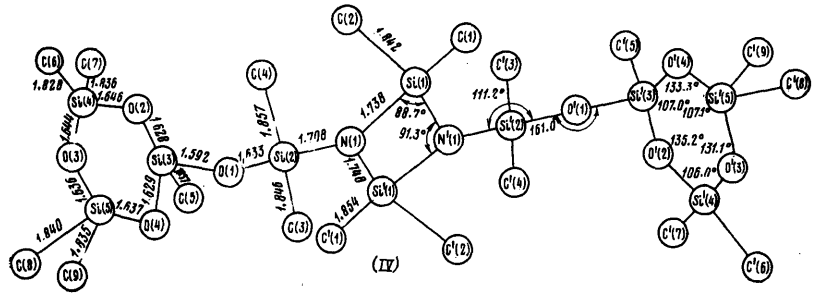


Figure 4. The molecular structure of 1,3-bis(2,2,4,4,6-pentamethylcyclotrisiloxanyloxydimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (IV).[16] The bond lengths (Å) and the valence angles (in degrees) are given on the left- and right-hand sides respectively.

has been refined by the method of least squares in terms of the full matrix anisotropic approximation up to $R = 0.038$ on the basis of 2866 reflections with $F^2 > 1.96\sigma$.

The molecule of compound (IV) is located at the centre of symmetry. The dihedral angle between the planes of the trisiloxane and disilazane rings is 21°. The bond lengths and angles in the cyclodisilazane (IV) molecule are presented in Fig. 4.[16]

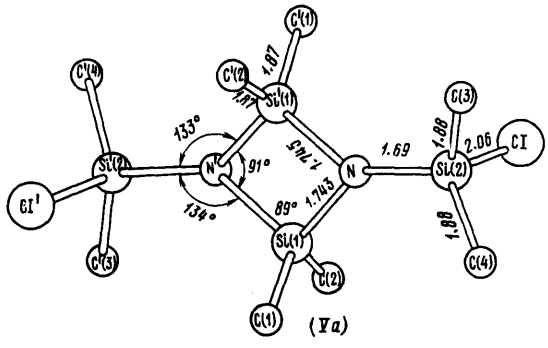


Figure 5. Stereochemistry of the 1,3-bis(chlorodimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (Va) molecule, bond lengths, and valence angles[18].

X-Ray diffraction study[17,18] of 1,3-bis(chlorodimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (Va) showed that crystals of this compound are monoclinic and have the lattice parameters $a = 6.653(3)$ Å, $b = 11.527(4)$ Å, and $c = 13.169(6)$ Å; $\gamma = 111.91(03)°$, space group $P2_{1/b}$, $Z = 2$. The structure has been elucidated by the direct method and has been refined by the method of least squares in terms of the anisotropic approximation up to an R factor of 6.9% using 1003 reflections. The four-membered disilazane ring is planar. No structural manifestations of the β-effect (the Cl → Si interaction) have been observed[18]. The bond lengths and valence angles are indicated in Fig. 5.

The amount of data available on the structure of phenylcyclodisilazanes is extremely small. Thus the crystal structure of 1,3-bis(chlorodiphenylsilyl)-2,2,4,4-tetraphenylcyclodisilazane (VI) has been determined[19] (Fig. 6). Crystals of compound (VI) are triclinic: $a = 11.192$ Å, $b = 12.016$ Å, $c = 9.707$ Å; $\alpha = 102.68°$, $\beta = 78.07°$, and $\gamma = 106.83°$. The structure has been refined up to an R factor of 10.6% on the basis of 1784 diffraction reflections with $I > 3\sigma$. It has been established that the crystals consist of a 1 : 1 solvate with benzene. The unit cell contains one formula unit, because both molecules are located at the centres of symmetry of the lattice (space group $P1$). The C(25), C(26), and C(27) atoms belong to the solvating benzene molecule located at the centre of symmetry (1/2; 1/2; 1/2).

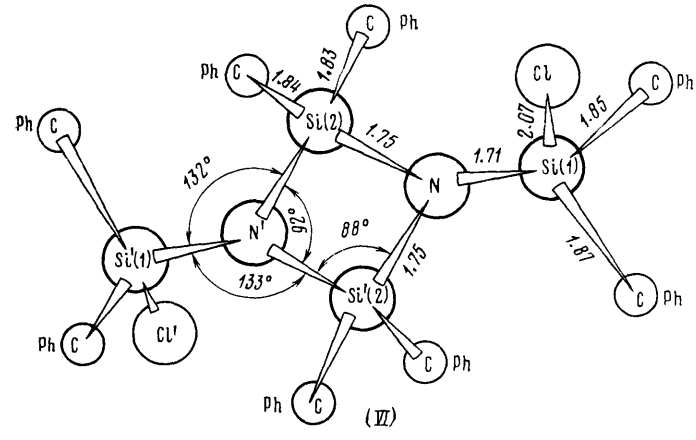


Figure 6. Stereochemistry of the 1,3-bis(chlorodiphenylsilyl)-2,2,4,4-tetraphenyldisilazane (VI) molecule, bond lengths and valence angles[19].

In conformity with symmetry requirements, the four-membered ring is planar. The Si–N bond lengths in the ring and the NSi(2)N′ and Si(2)NSi′(2) valence angles agree satisfactorily with other data[6,14]. The nitrogen atom has a nearly planar configuration (the sum of the valence angles is 357°), which indicates the delocalisation of its electron pair due to the d_π–p_π interaction with the Si(1), Si(2), and Si′(2) atoms. As in the previously investigated structures[4,14], the exocyclic Si(1)–N bond (1.713 Å) is shorter than the endocyclic Si(2)–N and Si′(2)–N bonds (1.746 and 1.750 Å respectively).

The observed Si(1)–Cl bond length, which is 2.072 Å, is appreciably greater than the normal value (2.01 Å);[20] nevertheless the compound exhibits an enhanced hydrolytic stability[17,19].

Thus the geometrical parameters of the molecules of the methyl- and phenyl-containing cyclodisilazanes (Va) and (VI) are in the main identical. The greatest differences were found on comparing the lengths of the exocyclic N–Si(R_2)Cl [1.690 Å for (Va) and 1.713 Å for (VI)] and Si–Cl [2.056 Å for (Va) and 2.072 Å for (VI)] bonds[18]. It is therefore impossible to observe a correlation between the differences in the reactivities and molecular geometries.

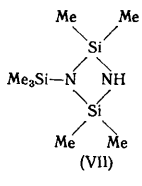
The infrared spectra of N-alkyl- or N-aryl-substituted cyclodisilazane have so far been inadequately investigated. It has been established that the nature of the substituents at the nitrogen atom affects the nature of the d_{π}–p_{π} bond and a corresponding shift of the region of asymmetric stretching vibrations of the Si–N bond in the Si(NSi) fragment of cyclodisilazane is observed[21–32].

The change in the nature of the organic group attached to the silicon atom[21] does not exert such an influence (Table 1).

Table 1. The influence of the nature of the organic group in the cyclodisilazane on the shift of the stretching vibration frequency ν_{as}[Si(NSi)] (cm^{-1}).[21]

Fragment	R					
	Me	Et	n-Pr	n-Bu	n-C_6H_{11}	Ph
$(Me_2Si—NR)_2$	912	955	—	923	953	963
$(RSiNHPh—NPh)_2$	—	917	917	919	—	—

As mentioned previously[4], *N*-substituted and particularly *N*-triorganosilyl-substituted organocyclodisilazanes are stable compounds. However, since the cyclodisilazane ring is highly strained, the replacement of one of the substituents at the nitrogen atom by hydrogen leads to the formation of chemically fairly reactive compounds[4,33], which is manifested by the anomalous disposition of the absorption bands due to stretching vibrations. Thus in the spectrum of 1-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane (VII)



(VII)

the nearest ν(NH) band shifts to 3510 cm^{-1} (which indicates an increased acidity of the proton attached to the N atom) and there is a corresponding shift of the central band to 1000 cm^{-1}. The ν(Si–N–Si) absorption band, corresponding to asymmetric stretching vibrations, which is believed[4,34] to characterise also the cyclodisilazane ring, is located in the region of 870 cm^{-1}.

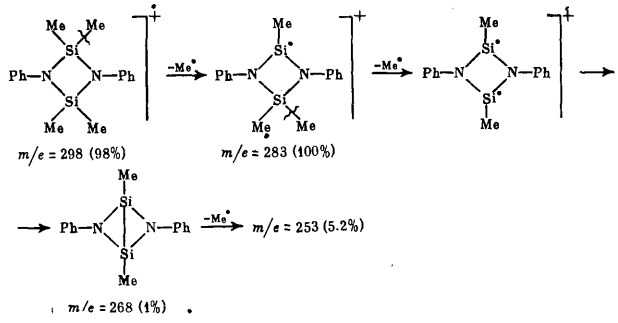
Analysis of the vibrational spectra of methylcyclodisilazanes showed[35] that vibrations due to individual Si–N bonds (endocyclic or exocyclic) cannot be isolated for the Si_4N_2 fragment (which can be treated to a first approximation independently of the vibrations of methyl groups and other functional groups attached to silicon atoms as a consequence of the so-called barrier effect of the silicon atom) and one must consider the vibrations of the fragment as a single whole. The wavenumbers 1050, 880, 770, 720, 460, and 430 cm^{-1} have been assigned to the stretching vibrations of the Si_4N_2 fragment. These wavenumbers do not in fact change as the functional groups at the silicon atom are varied. The bands in the region of 1050 cm^{-1}, which are intense in the infrared spectrum and are absent from the Raman spectrum, as well as the intense polarised bands in the region of 460 cm^{-1} in the Raman spectrum[35–37] can be specified as the most characteristic. It has been confirmed spectroscopically that the Si_4N_2 skeleton in 1,3-bis(chlorodimethylsilyl)-2,2,4,4-tetramethylcyclodisilazanes (Va) is planar, because the alternative prohibition rule holds for the stretching vibrations of the Si_4N_2 fragment, three of which (1050, 880, and 430 cm^{-1}) are active only in the infrared spectrum, while three others (770, 720, and 460 cm^{-1}) are active only in the Raman spectrum. This result agrees satisfactorily with X-ray diffraction data[17]. The deformation vibrations of the Si_4N_2 fragment are not considered, since they lie in the region of very low frequencies where their interpretation is difficult. Comparison of the spectra of liquids (melt at 100 °C) and crystals showed that significant changes are not observed in the transition from the liquid to the crystalline state[35].

The vibrational spectra of phenylcyclodisilazanes have been interpreted by comparison with the spectra of diphenylsilane. The majority of the vibrations of the benzene rings are characteristic either in terms of frequency or in terms of frequency and mode, which makes it possible to separate them from the vibrations of the Si_4N_2 fragment. In the Raman spectra the bands corresponding to the vibration of the benzene rings are much more intense than those due to the stretching vibrations of the Si_4N_2 fragment. The wavenumbers 1020, 800, 720, 610, 540, and 400 cm^{-1} have been assigned to the stretching vibrations of the Si_4N_2 fragment[38].

The intense infrared band in the region of 800 cm^{-1} can be specified as the analytical band for phenylcyclodisilazanes. The changes in the frequency of this band as a function of the functional groups attached to the exocyclic silicon atom are 798 cm^{-1} when H is replaced by OH, 800 cm^{-1} for Cl, 801 cm^{-1} for OEt, and 824 cm^{-1} for NH_2.[39]

The vibrational spectroscopic data are satisfactorily consistent with the planar structure of the four-membered silazane ring in 1,3-bis(chlorophenylsilyl)-2,2,4,4-tetraphenylcyclodisilazane (VI). The alternative prohibition rule holds for the ν(Si–N) stretching vibrations: the frequencies corresponding to vibrations of the B_{2u} and B_{3u} symmetry types (540, 800, and 1020 cm^{-1}) are active only in the infrared spectra, while the frequencies corresponding to the vibrations of the A_g and B_{1g} symmetry type (400, 610, and 720 cm^{-1}) are active only in the Raman spectra[38].

The mass spectra of *N*-alkyl- and *N*-aryl-cyclodisilazanes as well as the interpretation of the differences between the mass spectroscopic fragmentations of organocyclodisilazanes have been described[21,31,40,41]. A characteristic feature of the mass spectrum of compound (II) is the high (98%) intensity of the peak due to the molecular ion whose decomposition takes place via the consecutive loss of methyl groups[40]. The transitions $M^+ \rightarrow (M - Me)^+ \rightarrow (M - 2Me)$ have been confirmed by the presence of the corresponding metastable peaks.



The *m/e* 149 peak (Table 2) corresponds to the doubly charged molecular ion M^{2+} and not to the singly charged ion formed as a result of the decomposition involving the dissociation of two Si–N bonds. The dissociation of the bonds in the ring leads to rearranged ions with *m/e* 119 and 93:

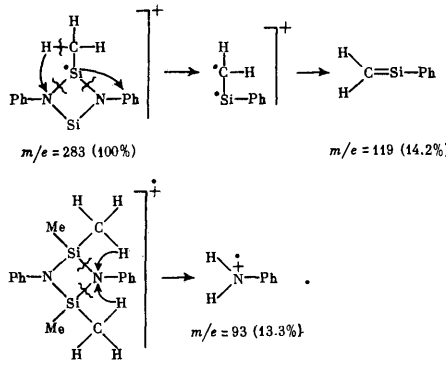
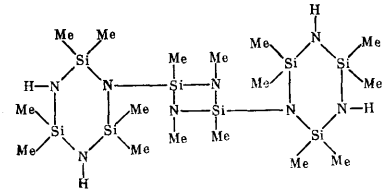


Table 2. Mass spectrometric data for 1,3-diphenyl-2,2,4,4-tetramethylcyclodisilazane (II).[40]

m/e	*I*, %	*m/e*	*I*, %	*m/e*	*I*, %	*m/e*	*I*, %
301	1.9	148	4.8	104	2.7	72	3.1
		147	4.1	101	3.8	71	5.2
300	13.4	137	7.7	100	13.4	70	9.9
299	36.7	127	5.8	99	1.9	69	7.4
298	98	126	7.6	96	2.5	60	3.8
297	2	125	5.7	95	5.7	59	21.1
286	1.7	124	4	94	3.8	58	15.4
285	12.9	123	7.2	93	13.3	57	7.2
284	25	122	5.8	92	3.7	56	7.6
283	100	121	5.6	91	9.1	55	7
268	1	120	7.5	86	4.4	54	5.7
254	1.2	119	14.2	85	5	52	1.9
253	5.2	118	3.8	84	12.5	51	4
225	3.3	111	3.6	83	5.8	45	12.8
194	1.1	110	3.4	82	2.9	44	3.8
193	1.7	109	3.5	78	3.7	43	48.1
192	1.6	108	2.3	77	9.6	42	3.7
191	1.7	107	3.7	75	5.4	41	7.7
150	3.8	106	3.8	74	7.7	40	19.2
149,5	3.9	105	3.9	73	23.1	39	7.7
149	21						

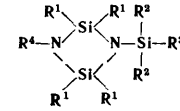
The mass spectrum of 1,3-dimethyl-2,4-bis(2,2,4,4,6,6-hexamethylcyclotrisilazanyl)-2,4-dimethylcyclodisilazane



is characterised by the following peaks: *m/e* 580 (6%) $[M]^+$; *m/e* 565 (49%) $[M - Me]^+$; *m/e* 548 (19%) $[M - Me, -NH_3]^+$; *m/e* 534 (100%) $[M - 2Me, -CH_2]^+$; *m/e* 519 (10%) $[M - 3Me, -CH_4]^+$; *m/e* 495 (9%), *m/e* 482 (15%), *m/e* 461 (14%), *m/e* 275 (12%).[41]

The principal ^1H NMR data for *N*-alkyl- and *N*-aryl-cyclodisilazanes have been published in a number of studies[2,22,26–28,41–53]. In the ^1H NMR spectra of cyclodisilazane derivatives of compound (Va) the chemical shift of the signals due to the protons in the methyl group linked to the silicon atom of the cyclodisilazane is $\tau = 9.76–9.79$; for the protons of the methyl groups linked to the exocyclic silicon atom, $\tau = 10.01–10.05$ (10% solution in CCl_4).[27,32] The following chemical shifts of the proton signals are characteristic of the ^1H NMR spectra of 1,3-dimethyl-2,4-bis(2,2,4,4,6,6-hexamethylcyclotrisilazanyl)-2,4-dimethylcyclodisilazane (solution in CH_2Cl_2, internal standard—$SiMe_4$):[41] $\tau = 9.96$ for the protons of the $SiMe_2$ group, $\tau = 9.89$ for the protons of $N(SiMe_2)_2$, $\tau = 9.83$ for the protons of SiMe, and $\tau = 7.43$ for the protons of NMe. The chemical shifts of the protons in the cyclodisilazane compounds with different organic groups are presented in Table 3.

Table 3. Chemical shifts of the proton signals of *N*-triorganosilyl-*N'*-organocyclodisilazanes (VIII)–(XI) [27,32]



Compound	R^1	R^2	R^3	R^4	$\tau_{(R^1)}$	$\tau_{(R^2)}$	$\tau^*_{(R^4)}$
(VIII)	Me	Me	Me	Me	9.85	10.04	7.55
(IX)	Me	Me	Me	Et	9.83	10.03	7.18 qu. 8.97 t.
(X)	Me	Me	Me	Ph	9.57	9.94	2.80—3.69 m.
(XI)	Me	Me	Ph	Me	9.87	9.72	7.53

*J = 7 Hz; notation: qu. = quartet, t. = triplet; m. = multiplet.

The chemical shift of the protons of the methyl groups linked to the endocyclic silicon atom is 9.85 for compound (VIII) and is intermediate between the values of τ for compound (Ia) (9.79) and 1,2,2,3,4,4-hexamethylcyclodisilazane (XII) (9.89), while the value for compound (XI) (9.57) is intermediate between 9.79 for compound (Ia) and 9.37 for compound (II).[26]

The photolysis of certain trialkylsilyl azides, such as trimethylsilyl azide or n-propyldimethylsilyl azide, results in the formation of cyclodisilazanes with different organic

groups[53]. Further photolysis of these cyclodisilazanes leads to the formation of high-molecular-weight alkylsilazanyl azides. The photolysis was carried out in a Rayonet reactor using Rayonet RPR-2737 lamps; the illumination periods ranged from 30 min to 65 h.[53]

There are no reports in the literature of systematic studies of organocyclodisilazanes by quantum-chemical methods. This is evidently because these methods have been introduced comparatively recently, but they permit a fairly correct analysis of the electronic structures of molecules. Quantum-mechanical methods have been used in terms of the approximation involving complete neglect of differential overlap and were not specially optimised for calculations on systems such as organocyclodisilazanes where the *d* atomic orbital of silicon plays a major role in the electronic structure and in which there is a marked charge separation in the Si–N bonds.

A version of the LCAO-MO SCF CNDO method[55] was used in one of the studies [54] and quantum-chemical calculations were made for cyclosilazanes. Compared with cyclosiloxanes, the quantum-chemical calculation for cyclosilazanes predicts a higher electron density at the silicon atom. As a result of the smaller charge separation in cyclosilazanes, the electrostatic component, which determines the dihedral angle involving the two silicon ring atoms, is smaller when the nitrogen atom is present at its vertex than in the compound with an oxygen atom. This is the cause of the formation of small SiNSi angles and relatively large SiOSi angles.

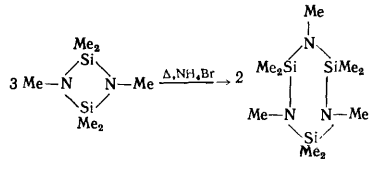
One of the factors which explains the cause of the stability of organocyclodisilazanes compared with organocyclodisiloxanes is the occurrence of strong additional endocyclic p_π–p_π interaction between opposite nitrogen atoms. The N...N bond index in cyclodisilazane is 0.478 a.u., which is approximately ten times greater than for the corresponding O...O interaction in cyclodisiloxane. In cyclosilazanes the extent of the N...N interaction diminishes rapidly with increasing ring size and in the eight-membered ring it already approaches the extent of the corresponding O...O interaction in cyclosiloxanes.

III. CHEMICAL REACTIONS AND PROPERTIES OF ORGANOCYCLODISILAZANES

1. *N*-Alkyl- and *N*-Aryl-Cyclodisilazanes

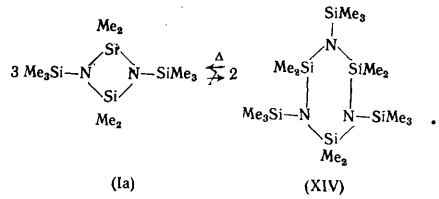
It has been shown by X-ray diffraction[4,14] that the angle between the bonds at the nitrogen atom in cyclodisilazanes is distorted and approaches the angle corresponding to pure *p* orbitals. This is manifested by a weakening of the endocyclic Si–N bond on passing from compound (XII) to compound (Ia).[8,24] However, although the reactivity of this bond should have increased in this direction, in reality it diminishes. Thus compound (XII) is readily solvolysed[56], while compound (Ia) is more stable in relation to water and alkalis[2]. The stability of cyclodisilazanes with methyl substituents at the silicon atom in relation to acids varies in the following sequence as a function of the substituents at the nitrogen atom: alkyl < trimethylsilyl < aryl.

Heating of compound (XII) or other *N*-methylated cyclodisilazanes in the presence of a catalyst leads to the irreversible formation of a six-membered silazane ring[24,57]:



(XII) (XIII) (1)

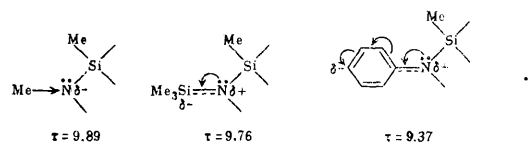
On the other hand, compound (Ia) and *N*-phenylcyclodisilazanes do not undergo a rearrangement under similar conditions[2]:



(Ia) (XIV) (2)

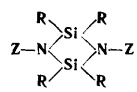
Compound (Ia) does not react with ammonium bromide [like compound (XII), which undergoes reaction (1)], while *N*-phenylcyclodisilazanes react only above 400 °C and very slowly, a mixture of products without a six-membered silazane ring being formed[2]. 1,3,5-Tris(trimethylsilyl)cyclotrisilazanes of type (XIV) are capable of being converted into cyclodisilazanes via reaction (2) at elevated temperatures (400–425 °C), but even at 450 °C the reaction does not go to completion[2].

The differences between the stabilities of cyclodisilazanes of different types can be accounted for by the different distributions of electron density in the molecule. Substituents at the nitrogen atom can increase or decrease the electron density as a result of the inductive influence. The reactions involving the Si–N bond, for example, hydrolysis, normally take place on protonation of the nitrogen atom and are facilitated by increasing nucleophilicity of the substituent. The electron density at the nitrogen atom and hence also the basicity decrease in the following sequence as a function of the substituent: Me > Me_3Si > Ph; the resistance of organocyclodisilazanes to electrophilic attack then increases. The d_π–p_π contribution to the Si–N bond in the ring decreases in the same sequence, which is confirmed by the changes in τ_{SiMe}:[2,8,24]



τ = 9.89 τ = 9.76 τ = 9.37

Table 4. Temperatures of the onset of decomposition of organocyclodisilazanes[58,59]



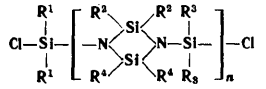
R	Z	*t*, °C	R	Z	*t*, °C	R	Z	*t*, °C
Ph	Me	392	Ph	Ph	455	Ph	*m*-C_6H_4F	418
Ph	Et	394	Me	*p*-$C_6H_5C_6H_4$	432	Ph	*m*-$(CF_3)_2C_6H_3$	384
Me	n-Bu	>223	Ph	*p*-$C_6H_5C_6H_4$	443	Me	$SiPh_2Me$	416
Me	C_6H_{11}	>317	Me	*m*-$C_6H_5OC_6H_4$	442	Me	$SiPh_3$	439
Me	Ph	481	Me	2,4,6-$(CH_3)_3C_6H_2$	365	Ph	$SiMe_3$	421

N-Phenyl- and *N*-trimethylsilyl-cyclodisilazanes exhibit a high thermal stability. An appreciable decomposition of the ring is not observed even at 450 °C.[58,59] Table 4 lists the temperature at which the test compounds lose 1% of their weight[58].

2. Reactions of α,ω-Diorganosilylcyclodisilazanes

The reactions of α,ω-diorganohalogenosilylcyclodisilazanes with electrophiles and nucleophiles, leading to different derivatives, are of great interest. In organocyclodisilazanes containing a chlorine atom in the side chain, for example, in compounds (Va)–(Vf), (VI), and (XV)–(XX) (Table 5), the latter is readily substituted by an organic group on treatment with an organometallic compound, for example, a Grignard reagent[27,34,60–63]. There is also a possibility of the replacement of only one Cl atom in compounds (XXII)–(XXIV) (Table 6) by selecting an appropriate reactant ratio[61,64]. The substitution of chlorine atoms by a triorganosiloxy-group can be achieved by allowing compounds of type (V) to react with the corresponding sodium triorganosilanoxides. The trimethylsiloxy- and methyldiphenylsiloxycyclodisilazanes (XXV) and (XXVI) obtained in this way are liquids; triphenylsiloxycyclodisilazanes (XXVII) are solids; oligomers with an odd number *n* are crystalline, while those with an even number *n* are waxy substances (Table 6).[61]

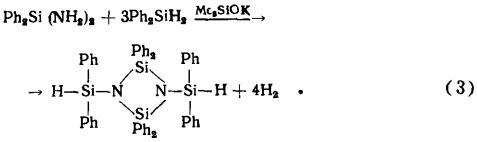
Table 5. Organocyclodisilazanes



Compound	*n*	R^1	R^2	R^3	R^4	B.p., °C/mmHg	M.p., °C	Refs.
(Va)	1	Me	Me	Me	Me	64/0.08	68–69	[27, 61–63]
(Vb)	2	Me	Me	Me	Me	118/0.05	43,5	[61, 64]
(Vc)	3	Me	Me	Me	Me	186/0.01	109–110	[61, 64]
(Vd)	4	Me	Me	Me	Me	248/0.01	93	[61, 64]
(Ve)	5	Me	Me	Me	Me	287/0.005	149–152	[61, 64]
(Vf)	6	Me	Me	Me	Me	315/0.005	147	[61, 64]
(VI)	1	Ph	Ph	Ph	Ph	—	260	[60]
(XV)	1	Ph	Ph	Me	Ph	282/0.05	283	[60]
(XVI)	1	Ph	Ph	Ph	Me	282/0.05	106	[60]
(XVII)	1	Ph	Me	Ph	Me	218/0.05	139	[60]
(XVIII)	1	Ph	Ph	Me	Me	218/0.05	*	[60]
(XIX)	1	Ph	Me	Me	Me	144/0.005	41	[60]
(XX)	1	Me	Ph	Me	Me	134/0.005	73	[60]

*$n_D^{36} = 1.5863$.

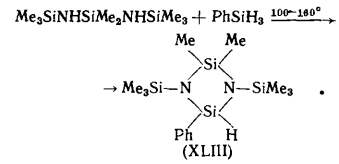
1,3-Bis(dimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (XXVIII) (Table 6) can be obtained from compound (Va) by reaction with lithium aluminium hydride[27,62,63] or by heating 1,1,3,3-tetramethyldisilazane in the presence of sodium methoxide or KOH;[65,66] 1,3-bis(diphenylsilyl)-2,2,4,4-tetraphenylcyclodisilazane (XLII) has been obtained by the interaction of diaminodiphenylsilane with diphenylsilane via reaction (3) using molar reactant ratios ranging from 1 : 3 to 1 : 4 in the presence of potassium trimethylsilanoxide as the catalyst[67,68].



(XLII)

(3)

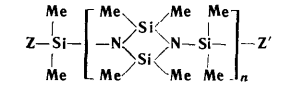
Dehydrocondensation can be used for the specific synthesis of organocyclodisilazanes containing a hydrogen atom at the endocyclic Si atom, for example[69]:



(XLIII)

The interaction of organocyclodisilazanes (V) with ammonia, amines, or amides leads to the formation of the corresponding nitrogen-containing cyclodisilazanes (XXIX)–(XXXV) (Table 6).[27,33,61–63,70,71] Other organocyclodisilazanes with the groups NH_2, NHR, or NR_2 (R = Me, Et, n-Bu, t-Bu, Ph, or $SiMe_3$) are obtained by the thermal condensation of organoaminosilanes $R_nSi(NHSiR'_3)_{4-n}$ (*n* = 0–2) or tetra-alkyl(aryl)-aminosilanes[72–76].

Table 6. Physical characteristics of organocyclodisilazanes

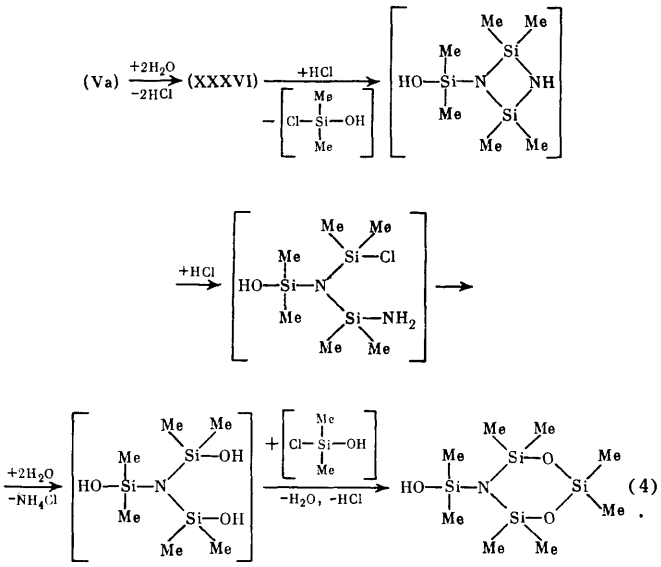


Compound	Z, Z′	*n*	B.p., °C/mmHg	M.p., °C	n_D^{20}	Refs.
(Ia)	Z=Z′=Me	1	85/7	39	1.4237*	[61]
(Ib)	Z=Z′=Me	2	104/0.005	20	1.4553	[61]
(Ic)	Z=Z′=Me	3	169/0.005	100	—	[61]
(XXIa)	Z=Z′=Ph	1	133/0.03	62	—	[61]
(XXIb)	Z=Z′=Ph	2	185/0.005	—	1.5093	[61]
(XXIc)	Z=Z′=Ph	3	275/0.02	—	1.535**	[61]
(XXIIa)	Z=Me; Z′=Cl	1	103/12	52	—	[61]
(XXIIb)	Z=Me; Z′=Cl	2	121/0.005	28	—	[61]
(XXIII)	Z=Ph; Z′=Cl	1	109/0.3	—	1.4892	[61]
(XXIV)	Z=*p*-$C_6H_5C_6H_4$; Z′=Cl	1	165/0.005	49	—	[61]
(XXVa)	Z=Z′=Me_3SiO	1	105/1	12	1.4227	[34, 61]
(XXVb)	Z=Z′=Me_3SiO	2	146/0.005	3	1.4425	[61]
(XXVc)	Z=Z′=Me_3SiO	3	205/0.01	18	1.4581	[61]
(XXVIa)	Z=Z′=$MePh_2SiO$	1	226/0.01	—	1.5338	[61]
(XXVIb)	Z=Z′=$MePh_2SiO$	2	274/0.001	39	1.5219	[61]
(XXVIIa)	Z=Z′=Ph_3SiO	1	—	189–191	—	[61]
(XXVIIb)	Z=Z′=Ph_3SiO	2	320–330/0.002	95***	—	[61]
(XXVIIc)	Z=Z′=Ph_3SiO	3	—	160	—	[61]
(XXVIII)	Z=Z′=H	1	73/10	—	1.4308	[27, 62, 63]
(XXIX)	Z=Z′=NH_2	1	108/12	36	—	[62, 63]
(XXX)	Z=Ph; Z′=NH_2	1	87/0.005	—	1.4880	[61]
(XXXI)	Z=Z′=NHMe	1	118/8	—	1.4518	[62, 63]
(XXXII)	Z=Z′=NMe_2	1	113–114/4	—	1.4530	[63]
(XXXIIIa)	Z=Z′=NEt_2	1	164/12	7–8	1.4584	[59, 63]
(XXXIIIb)	Z=Z′=NEt_2	2	152/0.01	−2	1.4675	[59]
(XXXIIIc)	Z=Z′=NEt_2	3	224/0.01	65	—	[59]
(XXXIIId)	Z=Z′=NEt_2	4	280/0.005	91	—	[59]
(XXXIV)	Z=Z′=NC_5H_{10}	1	142–144/0.1	42–43	—	[61]
(XXXV)	Z=Z′=NHPh	1	—	106–107	—	[63]
(XXXVI)	Z=Z′=OH	1	—	122–123	—	[27,62,63,80]
(XXXVII)	Z = Z′ = OMe	1	104–106/6	—	1.4368	[26, 62, 63]
(XXXVIII)	Z = Z′ = OEt	1	115–116/8	—	1.4342	[26, 62, 63]
(XXXIX)	Z = Z′ = OCH(CH$_3$)$_2$	1	85/1	—	1.4298	[63]
(XL)	Z = Z′ = OPh	1	147–149/0.02	44–45	—	[63]
(XLI)	Z = Z′ = $OCOCH_3$	1	95–97/0.2	49–52	—	[63]

*At 45 °C.
**At 50 °C.
***Reduced softening temperature.

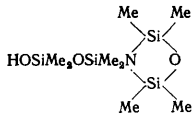
The hydroxycyclodisilazanes (XXXVI) (Table 6) and (XLIV) (Table 7) have been obtained by the hydrolysis of the organocyclodisilazanes (Va), (VI), (XV)–(XVIII), and (XXIX).[27,63,77–80].

The study of the hydrolysis of organocyclodisilazanes showed[77,78] that the composition of the final hydrolysis products of compounds (V) and (XXIX) is influenced not only by the acidity of the medium and the amount of hydrolysing agent, as in the hydrolysis of aminosilanes and silazanes, but also by the order of mixing of the initial components. The mechanism of the hydrolysis has been established:



The opening of the cyclodisilazane ring in the hydrolysis of compound (Va) can be apparently accounted for by the effect of the hydrogen chloride evolved in the first instant of the reaction, while the formation of the silazanesiloxane ring of 2,2,4,4,6,6-hexamethyl-5-hydroxydimethylsilyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane can be explained by the intermolecular condensation of the intermediates in reaction (4) under the influence of water.

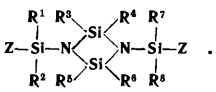
The initial and final compounds were analysed on the basis of mass spectrometric[81] and X-ray diffraction[79] data. The structure of the hydrolysis product of compound (XXXVI) was established on the basis of the observed behaviour[81]. The presence in the mass spectrum of this compound of the peak due to a molecular ion with *m/e* 295 and the peak of the ion $(M-Me)^+$ with *m/e* 280, which has the maximum intensity, indicates unambiguously the presence in the molecule of three oxygen atoms and one nitrogen atom. The high intensity (12%) of the peak of the $(M-MeOSiMe_2)^+$ ion with *m/e* 206 indicates the presence of the hydroxydimethylsilyl group at the nitrogen atom in the ring. The loss of the end group in decomposition following electron impact is not characteristic of linear siloxanes. This makes it possible to rule out the alternative structure with a four-membered ring



proposed by Fink[80] and to confirm the structure of the six-membered ring of 2,2,4,4,6,6-hexamethyl-5-hydroxydimethylsilyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane. Crystals of this compound (Fig. 7) are monoclinic with the lattice parameters $a = 6.866(2)$ Å, $b = 19.161(6)$ Å, and $c = 13.423(5)$ Å; $\beta = 105.25(10)°$, space group $P2_1/C$, $Z = 4$.

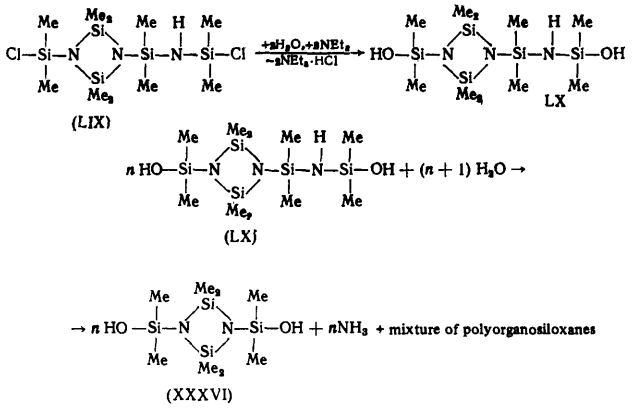
In the hydrolysis of 1-(3-chloro-1,1,3,3-tetramethyldisilazanyl)-3-chlorodimethylsilyl-2,2,4,4,-tetramethylcyclodisilazane (LIX) the reaction is influenced by the ratio of the amounts of the cyclodisilazane and the hydrolysing agent[82]; depending on the hydrolysis conditions, the product is either 1-(3-hydroxy-1,1,3,3-tetramethyldisilazanyl)-3-hydroxydimethylsilyl-2,2,4,4-tetramethylcyclodisilazane (LX) [reaction

Table 7. Physical characteristics of organocyclodisilazanes



Compound	Z	R^1	R^3	R^3	R^4	R^5	R^6	R^7	R^8	B.p., °C/mmHg	M.p., °C	n_D^{20}	References
(XLII)	H	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	—	224—225	—	[39, 67, 68]
(XLIV)	OH	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	—	158	—	[39, 60, 80]
(XLI)	NH_2	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	—	235—236	—	[39]
(XLVI)	OEt	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	—	—	1.5795	[39]
(XLVII)	Me	Me	Me	Ph	Ph	Me	Me	Me	Me	120/0.03	51	—	[60]
(XLVIII)	Me	Ph	Ph	Me	Me	Me	Me	Me	Me	124/0.005	—	1.5210	[60]
(XLIX)	Me	Ph	Ph	Ph	Ph	Me	Me	Me	Me	—	97	—	[60]
(L)	Me	Ph	Ph	Me	Me	Me	Me	Ph	Ph	—	144	—	[40, 60]
(LI)	Me	Me	Me	Ph	Ph	Ph	Ph	Me	Me	—	260	—	[60]
(LII)	Me	Ph	Ph	Ph	Ph	Me	Me	Ph	Ph	—	150	—	[60]
(LIII)	Me	Ph	Ph	Ph	Ph	Ph	Ph	Me	Me	—	215		[60]
(LIV)	$NH(C_3H_7)$	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	—	248—251	—	[60]
(LV)	NMe_2	Me	C_3H_4F	Me	C_3H_4F	Me	C_3H_4F	Me	C_3H_4F	140—142/0.1	80—85	—	[70]
(LVI)	NMe_2	Me	Ph	Me	Ph	Me	Ph	Me	Ph	206—210/0.01	—	1.5728	[70]
(LVII)	NMe_2	Me	$CH_2=CH$	Me	$CH_2=CH$	Me	$CH_2=CH$	Me	$CH_2=CH$	104—106/0.2	—	1.4849	[70]
(LVIII)	NMe_2	Me	Et	Me	Et	Me	Et	Me	Et	138—140/0.2	—	1.4722	[70]

(5)] or the products of its further transformation into a mixture of polyorganosiloxanes[82] [reaction (6)]:



(5)

(6)

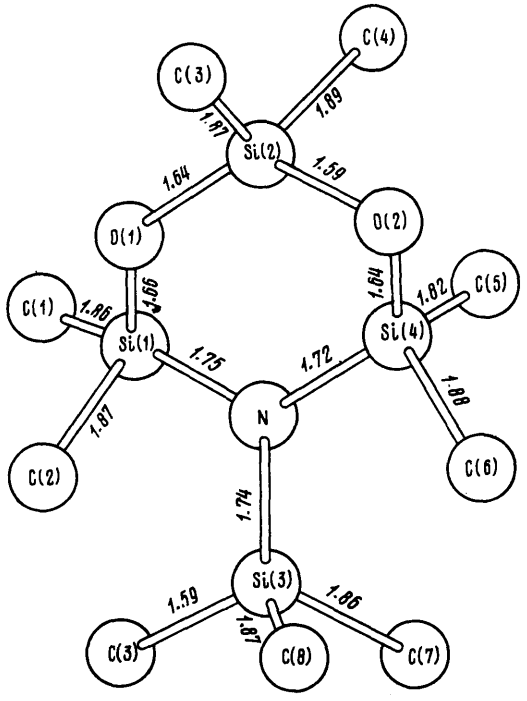
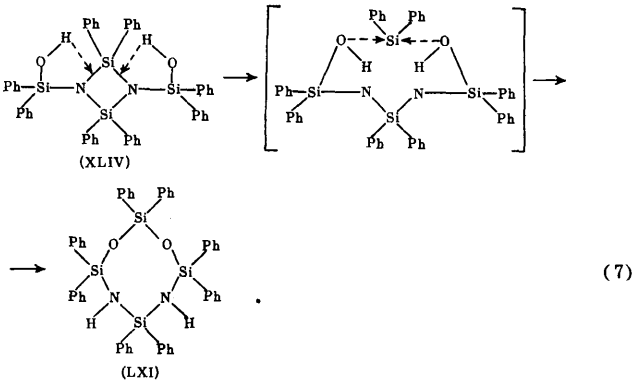


Figure 7. Stereochemistry of the 2,2,4,4,6,6-hexamethyl-5-hydroxydimethylsilyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane molecule[81].

In contrast to methylcyclodisilazanes, the hydrolysis of 1,3-bis(diphenylsilyl)tetraphenylcyclodisilazanes proceeds with retention of the cyclodisilazane ring regardless of the conditions[39].

The study of the influence of the functional groups (Cl, H, OH, NH_2, OEt), linked to the exocyclic Si atom in phenylcyclodisilazanes (VI) (Table 5) and (XLII)–(XLVI) (Table 7), on their hydrolytic stability showed that the hydrolysis involving the functional groups Cl and NH_2 takes place over a period of time and the final product is a mixture of the initial compound and the hydrolysis product, which is difficult to separate. Phenylcyclodisilazanes with the OEt of H substituents are hydrolytically stable under the same conditions[39].

Approximately 2–3% of 2,2,4,4,6,6,8,8-octaphenyl-1,3-dioxa-5,7-diaza-2,4,6,8-tetrasilacyclo-octane (LXI) was isolated in the separation of the hydrolysis products of phenylcyclodisilazane. Thus the hydrolysis of phenylcyclodisilazanes at the Si–X bond (X = Cl or NH_2) is accompanied to a slight extent by hydrolytic cleavage at the Si–N bond [reaction (7)] regardless of the conditions under which it takes place. Reaction (7) leads to the expansion of the four-membered cyclodisilazane ring[83]:

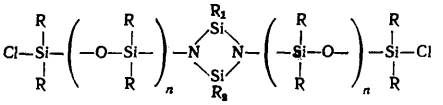


(7)

It is noteworthy that the separation of compounds (XLIV) and (LXI) presents considerable difficulties and can be achieved only by repeated recrystallisation from benzene. The presence of compound (LXI) decreases the melting point of compound (LXIV) from 157–158° to 141–150 °C.[83]

The structure of the product (LXI) was established by X-ray diffraction. The crystals of compound (LXI) are triclinic, belong to the space group $P\bar{1}$, and have the lattice parameters a = 14.912 Å, b = 13.258 Å, and c = 14.218 Å; α = 124.61°, β = 104.64°, and γ = 91.24°. The structure was elucidated on the basis of 2827 reflections and was refined up to an R factor of 11.6% (Fig.8).[83]

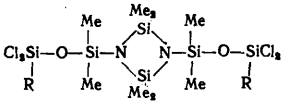
The hydrolysis of cyclodisilazane oligomers (LXII) yielded the corresponding α,ω-dihydroxy-derivatives[80,84,85], consisting of oily liquids:



(LXII)

R = Me, Et, CH_2 = CH or Ph; n = 1 – 3 .

The interaction of hydroxy-derivatives with trichloromethylsilane or trichlorophenylsilane in the presence of a hydrogen chloride acceptor gave rise to the tetrachloroderivatives (LXIII):[86]



(LXIII)

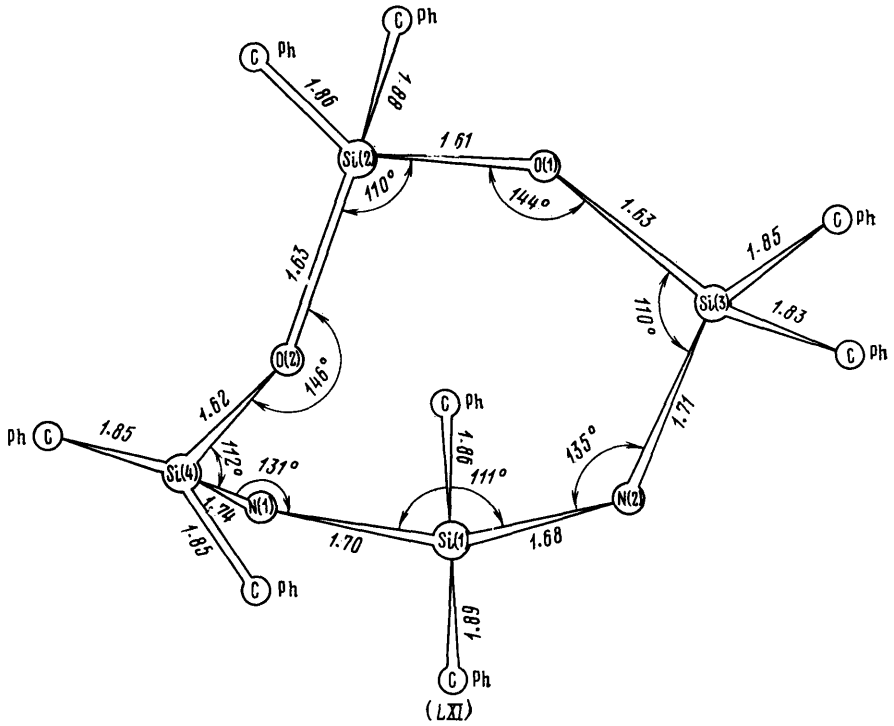
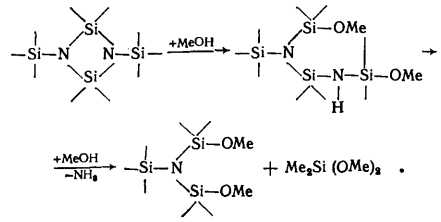


Figure 8. Stereochemistry of the 2,2,4,4,6,6,8,8-octaphenyl-1,3-dioxa-5,7-diaza-2,4,6,8-tetrasilacyclo-octane (LXI) molecule, bond lengths, and bond angles[72].

The interaction of organocyclodisilazanes with alcohols, phenol, and glacial acetic acid yielded the corresponding derivatives (XXXVII)–(XLI) (Table 6).[27,62,63]

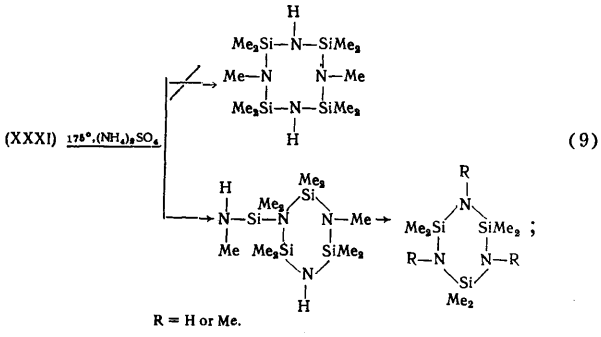
The alcoholysis of organocyclodisilazanes [reaction (8)] with a large (16-fold) excess of an alcohol, for example, methanol, cleaves the Si–N ring bond and symmetrical and asymmetrical silylamines are formed[26]:



(8)

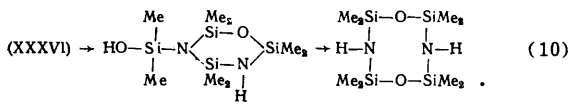
N,N'-Bis(diorganohalogenosilyl)cyclodisilazanes as well as the corresponding alkoxy- and phenoxy-derivatives (XXXVII)–(XL) (Table 6) remain unchanged on heating up to the boiling point in the presence of catalytic amounts of ammonium sulphate. Heating of 1,3-bis(dimethylaminosilyl)-2,2,4,4-tetramethylcyclodisilazane (XXIX) with ammonium sulphate (for 24 h at 200 °C) leads to a mixture of products, from which only hexamethylcyclotrisilazane was isolated (15%), although compound (XXIX) does not undergo any changes on refluxing (236 °C) without a catalyst[63].

It has been claimed[63] that, when 1,3-bis[dimethyl(methylamino)silyl]-2,2,4,4-tetramethylcyclodisilazane (XXXI) is heated to 175 °C with ammonium sulphate [reaction (9)], the ring expands and 1,2,2,4,4,5,6,6,8,8-decamethylcyclotetrasilazane is formed (38%). However, other workers[87] showed that this reaction results in the formation of a mixture of *N*-methylcyclotrisilazanes:



(9)

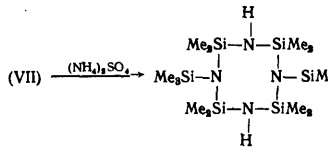
Andrianov et al.[88] showed that, on heating (1.5 h, 60 °C) in the presence of tetramethylammonium silanoxide (0.05%), compound (XXIX) undergoes reaction (10) and gives rise to octamethylcyclotetrasilazane (36%). A rearrangement with ring expansion is observed under the same conditions also for 1,3-bis(hydroxydimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (XXXVI):[88]



(10)

1-Trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane (VII) remains unchanged on heating, but in the presence of ammonium sulphate (1%) at 190 °C is converted via reaction

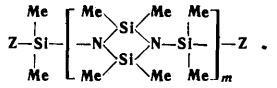
(11) into a dimer with an eight-membered ring[89]:



(11)

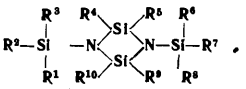
The characteristics of derivatives of oligomeric α,ω-diorganosilylcyclodisilazanes are presented in Table 6 and 7. Data for the thermal stabilities of certain organocyclodisilazanes[58] are given in Tables 8–10.

Table 8. Temperatures of the onset of decomposition of cyclodisilazanes[58]



m	Z			
	Me	Ph	$MePh_2SiO$	Ph_2SiO
1	503	>369	427	418
2	>340	422	419	419
3	462	426	—	418
5	459	—	—	—
7	395	—	—	—

Table 9. Temperatures of the onset of decomposition of cyclodisilazanes[58]



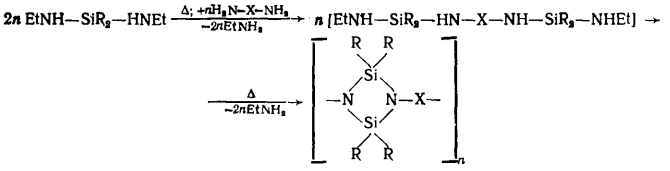
R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	*t*, °C
Me	Me	Me	Ph	Ph	Me	Me	Me	Ph	Ph	421
Ph	Me	Ph	Me	Me	Ph	Me	Ph	Me	Me	416
Me	Me	Ph	Me	Ph	Me	Me	Ph	Me	Ph	417
Me	Me	Me	Ph	Ph	Ph	Me	Ph	Me	Me	414
Ph	Me	Ph	Ph	Ph	Ph	Me	Ph	Me	Me	411
Ph	Me	Me	Ph	Ph	Me	Me	Me	Ph	Ph	418
Ph	Ph	Ph	Me	Me	Ph	Ph	Ph	Me	Me	439

IV. POLYMERS CONTAINING CYCLODISILAZANE UNITS

The polymers (LXIV) (Table 11) are usually synthesised in two ways—by the polycondensation of aromatic diamines with diaminosilanes and by the catalytic silylation of aliphatic or aromatic diamines by the organosilanes R_nSiH_{4-n}, where $n = 1$ and 2.

1. Polycondensation of Aromatic Diamines with Diaminosilanes

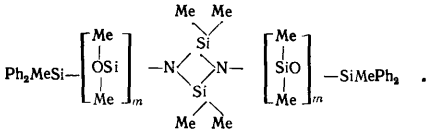
The polymers (LXIV, a–d) are formed via the following reaction with a reactant ratio of 2 : 1:[59,90]



(LXIV, a–d)

X=Ar; (Ia) — (Ib) : R=Me; (Id) : R=Ph; (12)
$n = 15 - 20$.

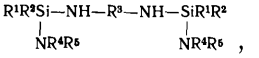
Table 10. Temperatures of the onset of decomposition of cyclodisilazanes[58]



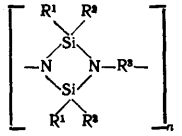
m	1	2	3	4
t, °C	427	417	413	411

N,*N'*-Alkylethyldiaminosilanes, whose amino-residue is readily split off, are used as the silyl component. Among aromatic diamines, derivatives with functional groups in the 1,4-, 3,3'-, and 4,4'-positions have been used. The formation of an intermediate via reaction (12) proceeds readily at 135–260 °C (depending on *R*); the cyclisation requires higher temperatures (~400 °C). The reaction can be carried out in the melt or in a high-boiling solvent, but neither method is altogether satisfactory, since the yield does not exceed 75%. Further reaction is prevented by the marked increase of viscosity or by the insolubility of the products as the degree of condensation increases. The degree of condensation obtained for compounds (LXIV, a–d) is therefore only 15–20.

By heating to a high temperature a compound

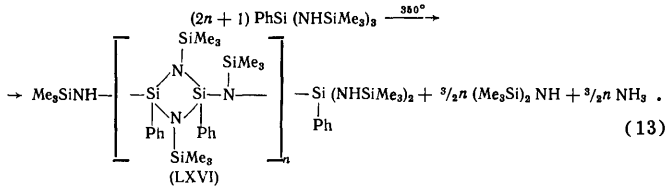


which is formed in its turn by heating a compound $R^4HNSiR^1.R^2NHR^4$ with a diamine $H_2NR^3NH_2$, one can obtain similarly the cyclodisilazane polymers (LXV), where R^1, R^2 = F, H, alkyl, alkenyl, alkynyl, cycloalkyl, or aryl [or R^1, R^2 = $-(CH_2)_m-$] and R^3 = arylene or a bivalent polyarylene oxide, polyarylene sulphide, or polyarylene sulphone residue[90–95]:



Solid not unduly brittle polymers with a slightly yellowish colour have been obtained. They are insoluble in various organic solvents and in water even after prolonged boiling. Such polymers do not melt up to 600 °C.

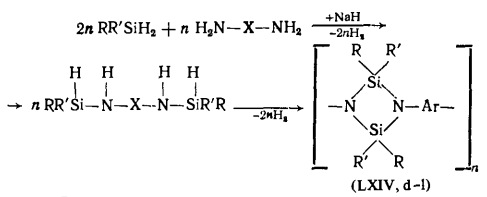
The thermal condensation of tris(trimethylsilylamino)phenylsilane leads to the formation of the oligomers (LXVI):[25]



(LXVI) (13)

2. Polycondensation of Aromatic and Aliphatic Diamines with Di- and Mono-organosilanes

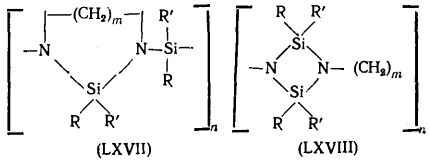
The polymers (LXIV, d–l) with a higher degree of polymerisation can be obtained by the catalytic silylation of primary aromatic diamines by di- and mono-organosilanes[59]:



(LXIV, d–l)

(LXIV, d–g); : R=R′=Ph; (LXIV, h–j); : R=H, R′=Ph;(LXIV, k and l): R= Me, R′=Ph . (14)

Reactions (14), catalysed by alkali metals or their hydrides, proceed very rapidly at 50–150 °C. Both polar (ether) and non-polar (benzene, xylene, etc.) solvents can be used. Only hydrogen is a side product of the reaction, the yield amounting to ~100%. The properties of the polymers (LXIV, d–l) are given in Table 11. α,ω-Polymethylenediamines condense with dihydro-organosilanes in the presence of catalysts (Na, K, NaH), forming polymers (LXVIII).[96] Fink[59] achieved the reactions of diphenylsilane with ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, and 1,6-diaminohexane at 30° to 85 °C with quantitative conversions of the initial reactants. Whereas the rigidity of the benzene residue in aromatic 1,4-, 3,3′-, and 4,4′-diamines clearly determines the structure of the polymers (LXIV) formed by reaction (14), the flexibility of the methylene chain in aliphatic diamines permits in this instance the formation of two isomeric polymers:

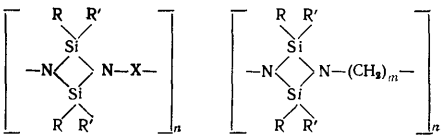


(LXVII) (LXVIII)

The polymethylene chain is either a component part of the ring as in formula (LXVII) or it links disilazane rings [see formula (LXVIII), Table 11].

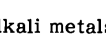
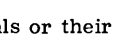
When the polymers (LXIV, a–l) are formed, they precipitate from the solution in the form of a light-coloured powder, which in most cases has a yellowish tint due to the charring of the amine. If the polycondensation is carried out in the melt, the polymers are obtained in a monolithic form with a very high viscosity. The polymers (LXVIII) are plastic and transparent. The solubility of the polymers (LXIV) in organic solvents is very low, with the exception of compounds (LXIVk) and (LXIVl); the polymers (LXVIII) readily dissolve in both aromatic and aliphatic solvents. The softening temperatures of some of the polymers (Table 11) lie above their decomposition temperatures, which can be explained by the reduced mobility and rigidity of the molecular chains[59].

Table 11. Cyclodisilazane polymers[59]



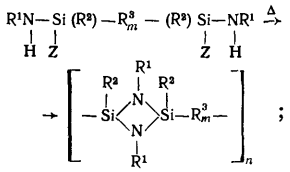
(LXIV, a–l), n=15–20 (LXVIII, a and b)

Compound	R	R′	X*	Softening temperature, °C	Structural unit
(LXIVa)	Me	Me	*A*	133	$C_{16}H_{20}N_2Si_2$
(LXIVb)	Me	Me	*B*	—	$C_{16}H_{20}N_2OSi_2$
(LXIVc)	Me	Me	*C*	—	$C_{22}H_{24}N_2O_2Si_2$
(LXIVd)	Ph	Ph	*A*	>315	$C_{36}H_{28}N_2Si_2$
(LXIVe)	Ph	Ph	*D*	>328	$C_{30}H_{24}N_2Si_2$
(LXIVf)	Ph	Ph	E	212	$C_{37}H_{30}N_2Si_2$
(LXIVg)	Ph	Ph	F	68	$C_{36}H_{28}N_2OSi_2$
(LXIVh)	H	Ph	D	>315	$C_{18}H_{16}N_2Si_2$
(LXIVi)	H	Ph	A	>315	$C_{24}H_{20}N_2Si_2$
(LXIVj)	H	Ph	E	>315	$C_{25}H_{22}N_2Si_2$
(LXIVk)	Me	Ph	A	117	$C_{26}H_{24}N_2Si_2$
(LXIVl)	Me	Ph	E	83	$C_{27}H_{26}N_2Si_2$
(LXVIIIa)	Ph	Ph	$-(CH_2)_4-$	61	$C_{28}H_{28}N_2Si_2$
(LXVIIIb)	Ph	Ph	$-(CH_2)_6-$	24	$C_{30}H_{32}N_2Si_2$

*Notation. *A*: ; *B*: ; *C*: ; *D*:  ;  ; *E*:  ; *F*:  .

The thermal stabilities of the polymers (LXIV) and (LXVIII) have been studied in very great detail[59]. The polymers (LXIV, d–g) decompose at 360–380 °C in an atmosphere of nitrogen. The aromatic residue linked to the ring nitrogen atom has only a very slight influence on the stability of the polymers. The decomposition temperature changes little also when the substituents at the silicon atom are varied [polymers (LXIV, a, d, i, and k)]. Whereas the temperature of the onset of the thermal decomposition of all the polymers investigated is independent of the nature of the organic framework around the silicon atom, the degree of weight loss depends markedly on the nature of the organic groups. Thus compounds (LXIV, f, i, and j) lose at 600 °C up to 30–35% of their initial mass and then do not decompose further. The thermal stability of compound (LXVIII) is low and depends markedly on the length of the methylene chain.

Thermostable cyclodisilazane polymers (LXIX) can be obtained by heating a tetrasubstituted aminodisilane:



(LXIX)

$m = 0, 1, n > 10,$

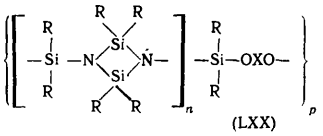
where Z is a primary amine residue, R^1 = alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, arylalkyl, alkylaryl, alkenylaryl, alkynylaryl, or aryl, R^2 represents the same

groups or OR^1, and R^3 = alkylene, alkenylene, alkynylene, arylalkynylene, biarylene, etc.[97-101]

Such polymers are pale-yellow resins, which melt at ~350 °C and are insoluble in the usual organic solvents and water.

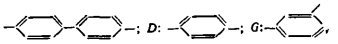
The polymers (LXX) ($p > 10$) (Table 12) are obtained by the polycondensation of cyclodisilazanes containing functional groups with bisphenols or bifunctional silanols. The α,ω-bis-(amino or chloro)silylcyclodisilazanes have been used as cyclodisilazanes with functional groups. The polycondensation is usually carried out in boiling xylene and the yield is 95–100% (calculated from the amount of amine evolved)[59,63,76,80,84-86,96-111].

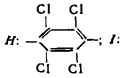
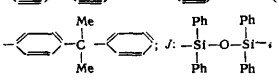
Table 12. Cyclodisilazane polymers[59]

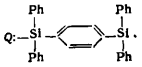


(LXX)

Compound	n	R	X*	Softening temperature, °C	Structural unit
(LXXa)	1	Me	*A*	330	$C_{20}H_{32}N_2O_2Si_4$
(LXXb)	2	Me	*A*	99	$C_{26}H_{50}N_4O_2Si_7$
(LXXc)	3	Me	*A*	127	$C_{32}H_{68}N_6O_2Si_4$
(LXXd)	4	Me	*A*	119	$C_{38}H_{86}N_8O_2Si_{13}$
(LXXe)	1	Me	*D*	90	$C_{14}H_{28}N_2O_2Si_4$
(LXXf)	1	Me	*G*	—	$C_{14}H_{28}N_2O_2Si_4$
(LXXg)	1	Me	*H*	238	$C_{14}H_{24}Cl_4N_2O_2Si_4$
(LXXh)	1	Me	*I*	145	$C_{23}H_{38}N_2O_2Si_4$
(LXXi)	1	Me	*J*	—	$C_{32}H_{44}N_2O_2Si_8$
(LXXj)	1	Ph	*A*	324	$C_{60}H_{48}N_2O_2Si_4$
(LXXk)	1	Ph	*Q*	101	$C_{78}H_{64}N_2O_2Si_6$

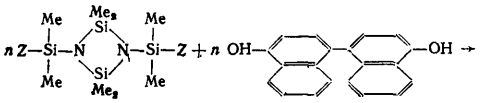
*Notation: *A*:  ; *D*: ; *G*: ;

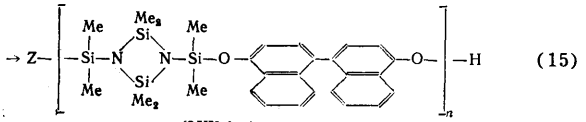
H:  ; *I*:  ; *J*: ;

Q:  .

The polymers (LXX, a–d) are white or yellowish elastic products; the softening temperatures of the polymers with an even number of cyclodisilazane units in the chain are lower than those of the polymers with an odd number of units. Their plasticity as well as their solubility in aromatic solvents increase with n. On passing from *p*-cresol and *m*-cresol to 2,2-bis(4-hydroxyphenyl)propane, the polymers (LXX, f–h) become more elastic. When the cyclodisilazanes are fully phenylated, the polymers (LXX, j and k) consist of white brittle compounds with an extremely low solubility in the usual organic solvents. The polymers (LXX, a, e, and f) are able to swell in hexane and benzene.

An interesting group of polymers (LXX, l–o) have been obtained by the low-temperature (up to 150 °C) and high-temperature (150–200 °C) condensation of cyclodisilazane monomers containing functional groups with 4,4'-dihydroxy-1,1'-binaphthyl:[112]



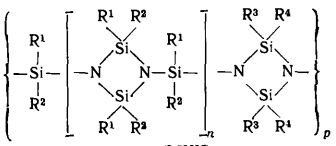


(LXX, l–o)

Z = Cl or NY; Y = H_2, Me_2, or HPh. (15)

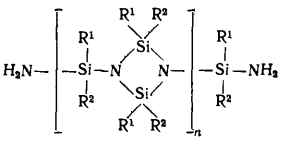
The polymers (LXX, l–o) have a molecular weight of the order of thousands, are thermally stable up to ~500 °C, are readily soluble in benzene or ethyl methyl ketone, and do not decompose on treatment with methanol, which indicates an increase of the stability of the cyclodisilazane ring in a macromolecular chain of this type[112].

Polymers containing the fully methylated cyclodisilazane are as a rule stable on heating to 430–440 °C in nitrogen. At this temperature the polymers begin to decompose slowly: rapid decomposition takes place at 510–560 °C. The stability of such polymers is not influenced either by the nature of the groups -OXO-, linking the silazane rings, or by the increase of the fraction of silazane rings in the polymers resulting from the incorporation of oligomeric cyclodisilazanes. In the case of the fully phenylated polymers (LXX, j and k) the decomposition does not begin until 500 °C, which is the absolute maximum for polymers with Si–N bonds.

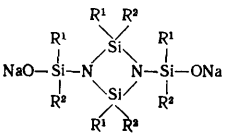


(LXXI)

The polymers (LXXI) are obtained by the interaction of α,ω-bisaminosilylated cyclodisilazanes



with the hydrosilanes $R^3R^4SiH_2$ (R^1, R^2, R^3, R^4 = H, F, a hydrocarbon group, or R^1R^2 and R^3R^4 = polymethylene group; n = 1–10) (molar ratio 2 : 1) in the presence of alkali and alkaline earth metals or their hydrides as catalysts[105,113-118], or by the condensation of the disodium or dilithium salts of 1,3-bis(diorganosilyl)cyclodisilazanes

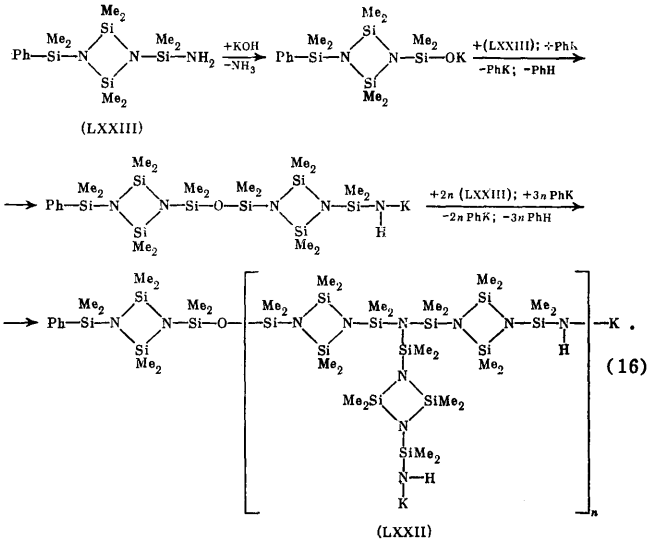


with dichlorodiorganosilanes $R^3R^4SiCl_2$ (with α,ω-dichlorodiorganosiloxanes) at 30–50 °C.[84,85,104,109,119,120]

The polymers (LXXI) are light-coloured brittle resins with softening temperatures in the range 80–100 °C. All the polymers (LXXI) obtained are thermally stable up to 450 °C.

The cyclodisilazane polymer (LXXII) with a branched structure has been obtained by the condensation of the monofunctional cyclodisilazane monomer (LXXIII) in the presence of KOH as the catalyst and without a solvent at 150–450 °C

in air or in an atmosphere of nitrogen at atmospheric pressure or *in vacuo*[112]:



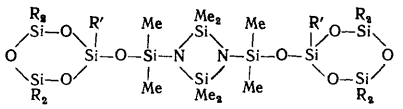
(LXXIII)

(LXXII)

(16)

The reaction is catalysed by potassium hydroxide introduced initially into the reaction and (as suggested by Deyak et al.[112]), by the phenylpotassium and potassium silanoxide formed in the reaction, each catalyst playing a specific role at different stages of reaction (16). A polymer of this type is readily soluble and exhibits a fairly high thermal stability (up to ~500 °C).

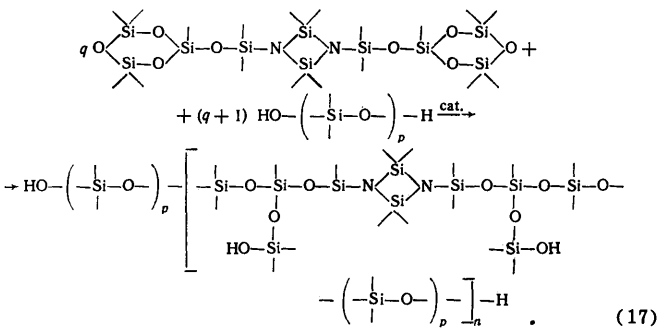
Anionic copolymerisation of cyclodisilazanes (LXXIV) [86]



(LXXIV)

R=R′=Me; R=Me, R′=Ph; R=Ph, R′=Me,

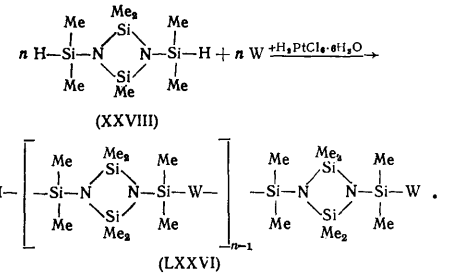
and α,ω-dihydroxypolydimethylsiloxanes also yielded branched cyclodisilazane polymers (LXXV).[121,122] The reaction is carried out in the presence of a catalytic amount of the diammonium or dipotassium salt of polydimethylsiloxanediol at 60–80 °C or at 140 °C respectively. The copolymerisation is based on the fact that the proton of the hydroxy-group exchanges for the catalyst cation, as a result of which the active centres are transferred from the catalyst to the organosilicon diol, which acquires the ability to interact with the cyclodisilazane (LXXIV), opening the siloxane rings in the latter and forming a polymer[121]:



(17)

A soluble polymer is formed in the initial stage of reaction (17) and then passes to a structured state (a three-dimensional network) with a high content of the insoluble product. Thermo-oxidative degradation of the polymers (LXXV) showed that the main decomposition reaction of these polymers proceeds in the range 400–450 °C.[121]

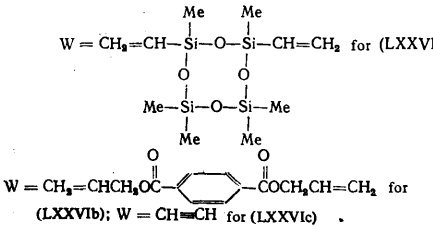
An interesting group of polymers (LXXVI) have been obtained by the reaction involving the polyaddition of 1,3-bis(dimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane to unsaturated organosilicon and organic compounds in the presence of chloroplatinic acid and rhodium compounds[123]:



(XXVIII)

(LXXVI)

The polymer (LXXVIa), with an intrinsic viscosity $\eta = 0.28$, is formed in the course of 3.5 h after the introduction of $H_2PtCl_2.6H_2O$ (1.5×10^{-5} M), in the form of a 0.1 M solution in tetrahydrofuran, into the equimolar mixture and on heating the reaction mixture to 170 °C. The reaction with diallyl isophthalate, leading to the formation of the polymeric product (LXXVIb), takes place under the same conditions in the course of 20–25 min up to a conversion of 98% when 1×10^{-4} M $H_2PtCl_6.H_2O$ is introduced into the equimolar mixture (η = 0.41 dl g^{-1}) or after 15–20 s up to a conversion of 100% in the presence of acetylacetonatorhodium dicarbonyl and rhodium carbonyl at concentrations of the rhodium compounds changing from 1×10^{-4} to 1×10^{-5} M, but under these conditions $\eta \leq 0.2$ dl g^{-1}. 1,3-Bis(dimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (XXVIII) reacts with acetylene at the normal pressure in an acetylene atmosphere at 170 °C and an $H_2PtCl_6.6H_2O$ concentration of 5×10^{-4} M. This results in the formation after 6 h of a viscous product (LXXVIc) (after reprecipitation from toluene, its yield is 90%), which sets on cooling and has a glass point of 153 °C.



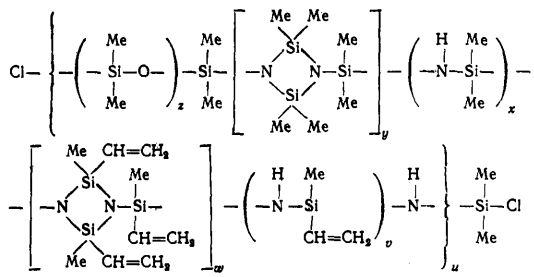
(LXXVIb); W = CH≡CH for (LXXVIc).

From the results obtained by Andrianov et al.[123], one may claim that 1,3-bis(dimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane is highly reactive, but apparently one of the most important conditions for the polyaddition reaction is the occurrence of the stage involving the formation of an intermediate in the presence of catalysts. This has been confirmed by the study of the dependence of the induction period on the reaction temperature and catalyst concentration[123]. A change in process conditions and of the catalyst concentration does not then influence significantly the rate of reaction.

The thermo-oxidative degradation of the synthetic polymers (LXXVI, a–c) has been investigated on a DO-102 derivatograph in air in the range from 20° to 800 °C at a heating rate

of 5 K min^{-1}. Comparison of the results of the thermogravimetric analysis (TGA) for the polymers (LXXVI, a–c) shows that the resistance of the carbo-organosilazane polymers (LXXVI, b and c) to degradation is lower than that of the polymer (LXXVIa) with alternating cyclodisilazane and cyclosiloxane fragments. Thus a weight loss of only 10% is observed at 350 °C for the polymers (LXXVI, b and c), while the same weight loss by the polymer (LXXVIa) is reached at 480 °C. The results of differential thermographic analysis (DTA) also indicate an increase of the resistance of the polymers to thermo-oxidative degradation after the introduction of cyclodisilazane fragments into the polymer chain. Thus the maximum rate of decomposition of polymer (LXXVIa) occurs at 570 °C.

The organosilazoxane polymers (LXXVII), containing cyclodisilazane and linear silazane fragments with terminal chlorosilyl groups, have been obtained by the thermal condensation of organocyclotrisilazanes with α,ω-dichlorodiorganosiloxanes [124,125]:

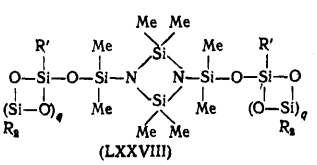


$z = 1-4$; $y = 1.8-2.5$; $x = 0.5-2.6$; $w = v = 0-0.2$; $u = 0-2$.

The authors[124,125] showed that the degree of reaction increases with increasing temperature and with enhancement of the electron-accepting properties of the substituents at the silicon atoms in the organocyclosilazane and also that the reactivity of α,ω-dichlorodiorganosiloxanes is almost independent of chain length. However, in the study of this reaction a complete transformation of the secondary nitrogen atoms in the cyclotrisilazane into the tertiary nitrogen atoms of the cyclodisilazane could not be achieved, so that the final reaction products contained the linear silazane fragments ≡Si–NH–Si≡. The course of the reaction was followed in all cases from the change in the content of the NH groups in the reaction mixture. The polymers obtained by the thermal condensation of 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilazane with α,ω-dichlorodiorganosiloxanes became subsequently structured, which may be accounted for by the partial polymerisation of the vinyl groups and the formation of a branched structure.

In order to eliminate low-molecular-weight products, the compounds (LXXVII, a–h) synthesised were evacuated to 5 mmHg at 200 °C, after which the content of active hydrogen was determined. The polymers (LXXVII, a–h) were identified from ^{1}H NMR and infrared spectroscopic data.

Polymers have been obtained[126] by the anionic polymerisation of tricyclic compounds (LXXVIII), whose molecules consist of two siloxane and one disilazane rings:



(LXXVIII)

$R = R' = Me$, $q = 2.3$; $R = Me$, $R' = Ph$, $q = 2$; $R = Ph$, $R' = Me$, $q = 2$.

The reaction takes place in the presence of the diammonium or dipotassium salts of polydimethylsiloxanediols at different temperatures in solution, in bulk, or in the solid state. The ratio of the soluble and insoluble fractions of the product then depends on the molecular structure of the initial compound (LXXVIII) and on its concentration.

Polymers with a branched macromolecular structure have been obtained[127,128] by the analogous reaction of 1,3-bis-(hydroxydimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (XXXVI) with hexamethylcyclotrisiloxane or octamethylcyclotetrasiloxane in the presence of tetramethylammonium siloxanedioxide with different initial reactant ratios. In both cases intramolecular rearrangements involving the expansion of both the disilazane and siloxane rings take place. This has been demonstrated by means of ^{1}H NMR spectra, in which a new peak due to methyl protons appears in a higher field than the peak of the methyl protons of the cyclodisilazane fragment; this new peak refers to the methyl protons in the trisilylamino-group of the expanded ring or the branched molecule[126]. The infrared spectra of such polymers were found to contain absorption bands in the range 930–950 cm^{-1}, characteristic of the Si–N bond and absent from the spectra of organocyclodisilazane compounds, as well as bands in the region of 1165, 1180, 3385, and 3420 cm^{-1}, characterising the deformation vibrations of the NH group and the stretching vibrations of the =N–H bond in the ≡Si–NH–Si≡ group[128].

The influence of the cyclodisilazane fragments on the hydrodynamic, conformational, and thermomechanical characteristics of polyorganosilazosiloxanes has been studied in relation to the products of the copolymerisation of 1,3-bis-(hydroxydimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane and hexamethylcyclotrisiloxane or octamethylcyclotetrasiloxane introduced into the reaction mixture in molar proportions of 1 : 25, 1 : 50, 1 : 75, and 1 : 100.[127,128] The authors expected that the introduction of the cyclodisilazane fragments into the polydimethylsiloxane chain should influence the flexibility of the macromolecular chain and ultimately the mechanical properties of the polyorganosilazosiloxanes.

In order to determine the hydrodynamic, conformational, and molecular parameters, all the polymers were fractionated in the benzene–dioxan system. The molecular weights were measured in CCl_4 on a Sofica photogoniodiffusometer (the refractive index increment $dn/dc = 0.05$; 25 °C; wavelength $\lambda = 5460$ Å). The intrinsic viscosities were measured in toluene at 25 °C and in ethyl methyl ketone at 20 °C. The Mark–Kuhn–Houwink equations for the first two polyorganosilazosiloxanes (molar ratios 1 : 25 and 1 : 50) $[\eta] = 2.04 \times 10^{-5} M^{0.86}$ and $[\eta] = 1.09 \times 10^{-5} M^{0.92}$ are close to the analogous equation for polydimethylsiloxane $[\eta] = 1.10 \times 10^{-5} M^{0.92}$ in toluene at 25 °C, while at 20 °C in ethyl methyl ketone the equation is $[\eta] = 9.99 \times 10^{-4} M^{0.49}$ for the second polyorganosilazosiloxane (1 : 50) and $[\eta] = 8.90 \times 10^{-4} M^{0.50}$ for polydimethylsiloxane.

Calculation of the unperturbed molecular sizes from the Fixman–Stockmayer equation (which makes it possible to eliminate the effect of long range action) yielded a value of K_θ for the second polyorganosilazosiloxane (1 : 50) in agreement with K_θ for polydimethylsiloxane[127]. The conformational parameters obtained indicate a virtually complete agreement between the flexibility parameters of polyorganosilazosiloxanes and polydimethylsiloxane. The authors[127] adopted the following geometrical parameters for the calculation of the conformational parameters: Si–N and Si–O bond lengths 1.73 and 1.65 Å respectively and 90° angles in the disilazane ring. Consequently the flexibility of the polyorganosilazosiloxanes obtained is close to that of polydimethylsiloxane and the chosen ratios of the cyclodisilazane and dimethylsiloxane

fragments do not have a significant influence on the properties of the polymers. An estimate of the hydrodynamic and conformational parameters of polydimethylsilazosiloxanes from data concerning their behaviour in dilute solution showed that their macromolecules have a predominantly linear structure[128]. For ratios of 1 : 25 and 1 : 50, a unimodal distribution was observed both on molecular weight distribution curves obtained by fractionation and on curves obtained by gel chromatography. This shows that the polymer specimens contained macromolecules of the same type. For ratios of 1 : 75 and 1 : 100, a bimodal distribution was observed on the molecular weight distribution curves, which is undoubtedly due to the formation of two types of macromolecule—with linear and branched structures.

V. APPLICATIONS OF ORGANOCYCLODISILAZANES

Comparative tests on the thermal stabilities of a series of cyclic and linear silazanes and silylamines showed that only four-membered cyclodisilazane compounds are stable at ~500 °C.[129] Furthermore, organocyclodisilazanes exhibit effective separating properties and a high solubility in organic solvents. The physical properties of cyclodisilazane polymers vary as a function of the nature of the substituents: certain polymers exhibit a high elasticity, others are elastic and rubber-like, those of a third kind are transparent, and polymers of the fourth kind are characterised by effective antiadhesion properties which facilitate the removal of castings from moulds. Cyclodisilazane polymers may find the same applications in many branches of industry as siloxanes and may prove to be actually more effective[109,130–134].

The vast majority of studies on organocyclodisilazane compounds have been published in the form of patents. A considerable proportion of the information contained in the latter is extremely indefinite although optimistic; a number of valuable properties characteristic of these compounds have been described.

The heat and frost resistance, effective dielectric properties, the absence of adhesion, and the exceptional resistance to atmospheric conditions made it possible to use organocyclodisilazanes in the manufacture of insulating materials for electric cables employed in important branches of industry such as aeroplane construction and automobile, electrotechnical, and chemical industries.

Materials based on organocyclodisilazanes possess a unique combination of properties such as flexibility at a low temperature, thermal stability, and resistance to hot engine oil. This results not only in an improvement of operating characteristics but also in an increased reliability of many components used in aeroplane, bus, and automobile engines (seals, cooling hose, washers, etc.).

The possibility of using organocyclodisilazanes as coatings for paper is of interest. A fairly large amount of such paper is necessary in the processing and packing of a wide variety of sticky materials such as untreated raw rubber or confectionery with a high sugar content; however, the most important application involves the preparation of backs of labels, decorative coatings, etc.

Further possible applications of organocyclodisilazanes should be noted: (1) as high-temperature liquid heat exchangers[64,135–143]; (2) as lubricants and as additives to lubricating oils[64,137,138]; (3) as thermostable film-forming coatings[99,101,105,115,116]; (4) as adhesion-improving coatings[117]; (5) as impregnating compounds for fabrics imparting thermal stability[99,105]; (6) as impregnating compounds imparting thermal stability to other materials[101,113,115,116]; (7) as components of fibre-forming materials imparting thermal stability to the latter[101,113,115,116]; (8) as reagents for the improvement of the properties of paper and mica[99,113]; (9) as auxiliary materials in the leather industry[113]; (10) as casting resins[90]; (11) as dyes resistant to heat and atmospheric conditions[99,101,105,113,115,116]; (12) in the manufacture of plastics[69,91,101,113,115,116].

In certain reports the use of organocyclodisilazanes as stabilising, structure-forming, and covulcanising agents has been mentioned. Apart from the possible applications of organocyclodisilazanes described above, isolated claims have been made in the patent literature concerning the good prospects for their application in other fields.

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During the preparation of the review for the press, a number of studies on organocyclodisilazanes were published.

It has been shown[144] that 1,3,2,2,4,4-hexaphenylcyclodisilazane forms monoclinic crystals with the lattice parameters $a = 10.471(2)$ Å, $b = 15.487(3)$ Å, and $c = 19.996(6)$ Å; $\beta = 108.06°$, $V = 3082.9(2.6)$ Å^3, $D_x = 1.178$, $Z = 4$, space group $C2/c$. The crystallographic twofold axis passes through the centre of the cyclodisilazane ring. The four-membered cyclodisilazane ring is not entirely flat: the dihedral angle, whose axis passes between two endocyclic Si atoms, is 1.2°. The *N*-phenyl fragments are almost coplanar with the plane of the cyclodisilazane ring (the dihedral angle between one of the halves of the cyclodisilazane ring and the phenyl group is 3.5°), demonstrating in its turn a characteristic feature of *N*-phenylcyclodisilazane derivatives, which consists in a favourable partial overlap of the π-electron system of the phenyl group with the unshared pair of *p* electrons of the nitrogen atom.

The crystal and molecular structures of 1,3-bis(chlorodimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane have been examined in detail[145]. The principal structural parameters of the molecule agree satisfactorily with previous values.

The ^{1}H NMR, NMR, and infrared spectra of monomeric organocyclodisilazanes incorporating various groups (Me, Et, CH_2=CH, iso-Pr, F, Cl) have been published[146–150].

Reactions involving the hydride addition of 1,3-bis(dimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane to pentamethylvinylcyclotrisiloxane and heptamethylvinylcyclotetrasiloxane in the presence of chloroplatinic acid (0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in tetrahydrofuran; 0.5×10^{-5} g-atom Pt per litre of mixture) have been investigated[151] and mono- and di-addition products have been isolated.

The α,ω-bis(chlorodimethylsilyl)cyclodisilazane oligomers containing between 2 and 5 cyclodisilazane fragments in the molecular chain have been formed by the reaction of equimolar amounts of hexamethylcyclotrisilazane and dichlorodimethylsilane and characterised[152]. The hydrolysis of these oligomers[153] and the hydrolysis of oligomers containing the cyclosiloxane ring in addition to the cyclodisilazane fragment[154] have been investigated.

Oligomers with different lengths of the molecular chain have been obtained by the thermal condensation of tetrakis(trimethylsilylamino)silane[155], or 1,3-bis(hydroxydimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane[156], or 1,3-bis(aminodimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane[156], or α,ω-dichlorodiorganosiloxanes with organocyclodisilazanes[157]. An interesting group of oligomers have been obtained as a result of the anionic polymerisation of oligo-organocyclodisilazanes incorporating siloxane rings in the presence of the diammonium or dipotassium salts of polydimethylsiloxanediols[158] and also via the interaction of oligoamino-organocyclodisilazanes, dimethylsiloxane, diphenylsiloxane, and butadiene oligomers containing terminal hydroxy-groups[159].

The ammonolysis and aminolysis of chlorine-containing organocyclodisilazanes, which leads to monomeric and dimeric reaction products with amino-groups, have been studied in detail[160,161]. The composition and structure of the ammonolysis products are significantly influenced by the nature of the solvent employed and of the groups attached to the silicon atom.

It has been established that the interaction of methylcyclodisilazanes with anhydrous hydrogen chloride proceeds with dissociation of endocyclic Si–N bonds and the opening of the cyclodisilazane ring, while the interaction of phenylcyclodisilazanes takes place only via the functional groups with retention of the cyclodisilazane structure[162].

In the study of the alcoholysis and acidolysis of 1,3-bis(diorganosilyl)tetraorganocyclodisilazanes it was found that the mode and rate of these reactions are influenced significantly by the electronic nature of the organic and functional groups attached to the silicon atoms and also by the ratio of the initial reactants[163,164].

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Reductive Polyheterocyclisation—New Method of Preparation of Polyheteroarylenes

V.V.Korshak, A.L.Rusanov, and D.S.Tugushi

Reduction and cyclisation of *o*-nitro-substituted heterochain polymers provides a new method for obtaining polyheteroarylenes of cyclochain structure. A large number of reactions demonstrate synthetic possibilities and show its advantages over traditional methods. A list of 90 references is included.

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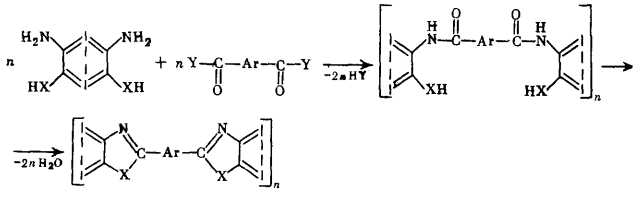
I. INTRODUCTION

The intense development of several modern industries—aviation, electronics, electrical technology, etc.—has made it necessary to produce polymeric materials combining high resistance to deformation with the ability to withstand prolonged operation at high temperatures. Solution of this problem is most directly related to the elaboration of new thermostable polymers, so that this has become a dominant trend in the development of the chemistry of macromolecular compounds during the past two decades[1-4].

The greatest progress in this field has been made in the development of polyheteroarylenes of cyclochain structure, compounds of high molecular weight containing in the main chains of the macromolecules alternating carbocyclic and heterocyclic aromatic ring systems[1-4]. Intense research on the synthesis of such polymers, undertaken in the USSR and abroad, has yielded a large number of products of this type, but only aromatic polyimides have become at all widely used[5,6], together with a few related systems made at present on an industrial or a semi-industrial scale. The overwhelming majority of polyheteroarylenes other than polyimides have not emerged beyond academic research or limited production on pilot plants. Yet many of these systems possess several important potential advantages over polyimides with respect to thermal and chemical stability, processability into articles, etc.

In most cases industrial exploitation of developments in the synthesis of polyheteroarylenes is difficult owing to the relative inaccessibility and inadequate stability of the initial monomers. A substantial obstacle is also the complexity of the technology involved in the principal methods for obtaining polyheteroarylenes, among which the most important are high-temperature polycyclocondensation in polyphosphoric acid[7-10], reaction in the melt followed by high-temperature solid-phase polycyclocondensation (Marvel's reaction),[11-13] and a multistage reaction involving a first stage under mild conditions, isolation of prepolymers, and their processing into articles followed by high-temperature cyclisation of the ready-made articles[1-6]. In the majority of cases the cyclisation stages are accomplished under severe conditions: the temperature usually exceeds 300 °C, which not only requires the use of special apparatus but also permits the occurrence of secondary processes—cross-linking, degradation, etc.—that have an unfavourable influence on the properties of the final products.

Typical examples of polyheteroarylenes are polybenzazoles[14-18]—a large family of thermostable polymers formed by reaction between *oo'*-disubstituted aromatic diamines and aromatic dicarboxylic acids or their derivatives:

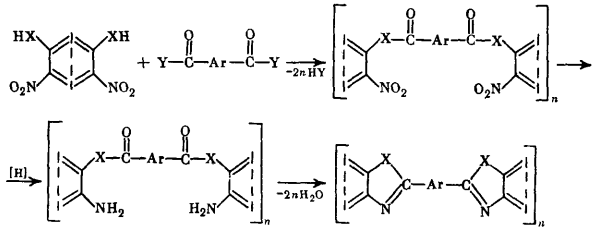


X = O, NR; Y = OH, OR', Cl; R = H, Alk, C_6H_5; R' = Alk, C_6H_5 . (1)

Replacement of the diamines by more accessible and stable monomers, and also elaboration of a technical method for synthesising these systems, may stimulate further development of the chemistry and technology of polybenzazoles. One solution to these problems is to synthesise them by reductive polyheterocyclisation.

II. REDUCTIVE POLYHETEROCYCLISATION

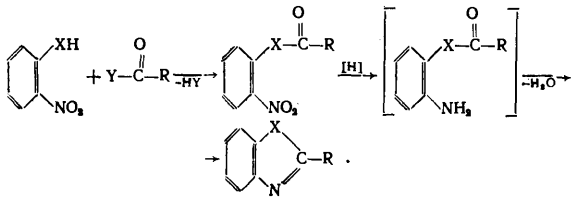
The synthesis of polybenzazoles by reductive polyheterocyclisation[19-28]



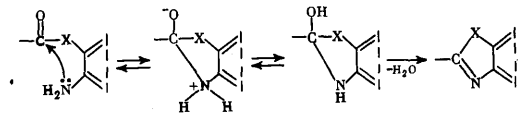
X = O, NR; Y = OR', Hal; R = H, C_6H_5, Alk; R' = Alk, C_6H_5 (2)

is based on well known reactions[29-31] in which benzazoles are formed by interaction of o-nitro-substituted amines and phenols with derivatives of carboxylic acids followed by

reduction and cyclisation of the products



Comparison of reductive polyheterocyclisation (2) with the traditional method (1) indicates that the former has several important advantages for the synthesis of polybenzazoles—(i) the use, instead of *oo'*-disubstituted aromatic diamines, of *oo'*-dinitro-substituted difunctional compounds, which are intermediates in the synthesis of the former[32], more accessible, cheaper, and more stable; (ii) the possibility of effecting the initial stages—synthesis of *o*-nitro-substituted heterochain polymers[19-28,33]—in the absence of competing reactions of acylation at two adjacent groups with branching and subsequent cross-linking of macromolecules[34,35], which permits the use as acylating agents of the most reactive derivatives of dicarboxylic acids, in particular their dichlorides; (iii) the possibility of using hydrogen chloride evolved as by-product in the early stages (when acid dichlorides are used as acylating agents) together with various metals, primarily activated iron[36], to reduce nitro to amino; and (iv) the possibility of using hydrogen chloride to catalyse polycyclisation[37,38], as a consequence of the increased electrophilic reactivity of the carbon atom in a protonated carbonyl group[39]

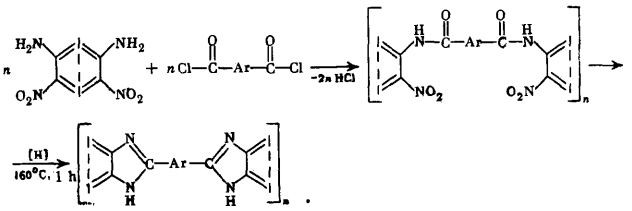


which enables the temperature of cyclisation to be lowered to 150–170 °C, with the possibility of ring-closure immediately after reduction of nitro to amino (which was responsible for the name *reductive polyheterocyclisation* for the whole process).

On the other hand, the process may be complicated by the possibility of incomplete reduction of nitro-groups and incomplete cyclisation of reduced and unreduced fragments, leading to an enhanced heterounit character of the polymers[39,40], which lowers the thermal stability, heat resistance, and chemical stability of the final products.

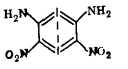
For maximum exploitation of the positive aspects of reductive polyheterocyclisation and elimination of inherent potential disadvantages it is advisable that all stages of the synthesis of polybenzazoles should be conducted as a continuous process in *N*-methylpyrrolid-2-one—an effective solvent for heterochain and heterocyclic polymers—with reduced iron and hydrogen chloride as reducing agents, the latter also catalysing cyclisation. Solubility of polymers at all stages of synthesis is especially important in reductive polyheterocyclisation, since polymers that separate out at any stage coat the iron and thus remove it from the sphere of reaction.

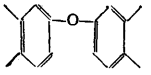
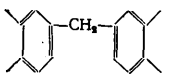
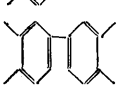
The presence in the monomers of nitro-groups, which are strongly electron-accepting substituents, has a decisive influence on the reactivity of fragments involved in polycondensation. In particular, the electronic and steric effects of *o*-nitro-substituents produce a sharp decrease in basicity and hence in nucleophilicity of diamines[20-22], and limit the possibility of using various bis-*o*-nitroanilines to obtain polybenzimidazoles by the reaction series



The highest (73 ± 3%) yields of dibenzimidazoles from bis-*o*-nitroanilines and benzoyl chloride are obtained[41] by the use as monomers of bis-*p*-amino-*m*-nitrophenyl ether and *mm'*-dinitrodiphenylmethane-*pp'*-diamine, which quantum-chemical calculations of potentiometric titration[21,22] show (Table 1) to be the most basic among the bis-*o*-nitroanilines used. The comparative basicity sequences of these latter compounds (Table 1) are identical with those of the structurally similar unsaturated aromatic diamines[42,43], among which the more basic are bis-*p*-aminophenyl ether and diphenylmethane-*pp'*-diamine. The comparatively high basicity of bis-*o*-nitroanilines containing ether and methylene bridging groups and also the high yields of dibenzimidazoles obtainable from them made it advisable to use such compounds for the synthesis of polybenzimidazoles. Another factor favouring their use in reductive polyheterocyclisation is the better solubility of the resulting polymers than of systems based on 3,3'-dinitrobenzidine and 4,6-dinitrophenylene-1,3-diamine, which enables the synthesis to be conducted in homogeneous solutions.

Table 1. Basicity and electron densities on nitrogen atoms for initial and monoacylated d_N^0 and d_N^m bis-*o*-nitroanilines of general formula[22]

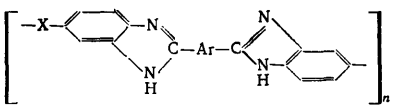


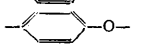
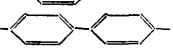
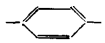
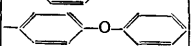
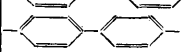
	pK_a (in dimethylformamide)			d_N^0	d_N^m
	pK_{a_1}	pK_{a_2}	ΔpK_a *		
	2.64±0.20	1.81±0.20	0.83	1.785	1.690
	2.57±0.20	1.87±0.20	0.70	1.782	—
	2.35±0.20	1.59±0.20	0.76	1.775	1.680
	2.17±0.20	1.17±0.20	1.00	1.751	1.61

*Here and subsequently $\Delta pK_a = pK_{a_1} - pK_{a_2}$.

The structure of the acid dichlorides imposes no severe restriction on their use to obtain polybenzimidazoles: model compounds are obtained in high (80 ± 6%) yields from all acid dichlorides[41], but isophthaloyl and oxy-*pp'*-dibenzoyl chlorides are preferred as monomers, since the resulting polymers remain in solution at all stages of the synthesis. Furthermore, the weak electrophilicity of these compounds[44] is responsible for the diminished positive charge on the amide carbon atoms and the consequent greater resistance to hydrolysis and amidolysis during reductive cyclisation.

Table 2. Some characteristics of polybenzimidazoles of general formula[22]

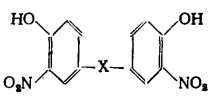


X	Ar	Solubility in *						Decomp. temp., °C**
		MP	DMA	$C_2H_2Cl_4$ + C_6H_5OH	HCOOH	CF_3COOH	H_2SO_4	
O		+	+	+	+	+	+	440
O		±	±	±	±	+	+	445
O		+	+	+	+	+	+	440
O		±	±	±	±	+	+	450
CH_2		+	+	+	±	+	+	420
CH_2		±	±	±	±	+	+	430
CH_2		+	+	+	+	+	+	425
CH_2		±	±	±	±	+	+	440

*MP = *N*-methylpyrrolid-2-one; DMA = dimethylacetamide; + = soluble at room temperature; ± = soluble on heating.

**Temperature at which 5% of initial weight has been lost (differential thermogravimetric analysis, $\Delta T = 4.5$ deg min^{-1}, air).

Table 3. Acidity of bis-*o*-nitrophenols of general formula[26]

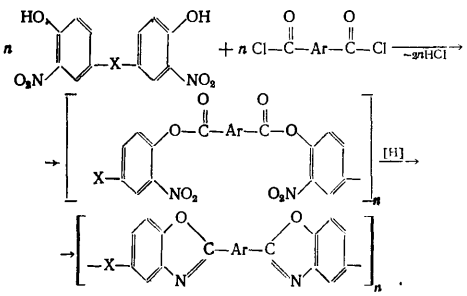


X	pK_{a_1}	pK_{a_2}	ΔpK_a
SO_2	5.80	7.50	1.70
$C(CF_3)_2$	7.54	9.14	1.60
O	9.17	10.93	1.76
$C(CH_3)_2$	9.53	11.11	1.59
$-CH_2-$	9.73	11.22	1.69

The synthesis of polyimidazoles by reductive polyheterocyclisation is a simple and technically efficient process involving addition of a solid acid dichloride to an *N*-methylpyrrolid-2-one solution of a bis-*o*-nitroaniline, stirring for 10–12 h, saturating the solution with gaseous hydrogen chloride, and heating in a stream of nitrogen and hydrogen chloride at 160 °C for 1 h. The infrared spectra of polybenzimidazoles obtained in this way from isophthaloyl and oxy-*pp'*-dibenzoyl chlorides, i.e. with all stages taking place in solution, contain no absorption maxima that would indicate incomplete reduction of nitro-groups or polycyclodehydration. Table 2 lists several characteristics of these polymers.

The attainment of high degrees of cyclisation under very mild conditions (160 °C for 1 h) is one of the most important merits of reductive polyheterocyclisation. Furthermore, such conditions tend to suppress any secondary reactions and yield polymers having the same thermal stability as those obtained by traditional methods, but better solubility in organic solvents (Table 2) and lower softening temperatures. Thus catalytic cyclisation not only permits substantial moderation of the conditions for obtaining polybenzimidazoles but also yields polymers having better properties.

These considerations apply also to the production of polybenzoxazoles by the reactions[23–28,33]



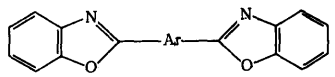
The acidity of the bis-*o*-nitrophenols used for the synthesis of polybenzoxazoles varies within wide limits (Table 3). but it is not the limiting factor in the choice of monomers. Thus model reactions show that high yields of bisbenzoxazoles are obtained from all bis-*o*-nitrophenols[45], so that attention has been concentrated on obtaining polybenzoxazoles from the most readily available 3,3'-dinitrodiphenylmethane-4,4'-diol and 2,2-bis-(4-hydroxy-3-nitrophenyl)propane, which furthermore ensure homogeneous solutions during reductive polyheterocyclisation, together with isophthaloyl and oxy-*pp'*-dibenzoyl dichlorides.

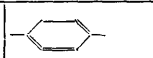
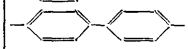
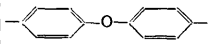
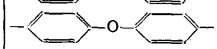
The procedure for obtaining polybenzoxazoles is essentially the same as that described above for polybenzimidazoles, except that the first stage—formation of poly-*o*-nitroesters—is accomplished in the presence of triethylamine, and the duration of the process does not exceed 30 min. The properties of the resulting polybenzoxazoles, shown by infrared spectroscopy to contain no "defective" monomer units, are given in Table 4. They differ from those obtained by traditional methods[46,47] in their solubility in trifluoroacetic acid, while systems containing isopropylidene groups are soluble in a 3:1 mixture of tetrachloroethane and phenol. The high viscosity characteristics of polybenzoxazoles, evidence of high molecular masses, are responsible for their film-forming properties.

When difficulties arise in obtaining *o*-nitro-substituted monomers or polymers, the required compounds can be produced by nitrating the corresponding unsubstituted heterochain polymers. Thus the nitration of aromatic polyamides[22], polyesters[48], and polythioesters[49] yields macromolecular poly-*o*-nitroamides, poly-*o*-nitroesters, and poly-*o*-nitrothioesters, reductive polyheterocyclisation

of which then gives polybenzimidazoles[22], polybenzoxazoles[48], and polybenzothiazoles[49]. However, the nitration of heterochain polymers may be ambiguous (i.e. it may not necessarily take place *ortho* to the main chains of the macromolecules), which leads to the formation of heterounit polymers[40], and furthermore such nitration is accompanied by a considerable decrease in viscosity.

Table 4. Some characteristics of polybenzoxazoles of general formula[26]



X	Ar	Softening temp., °C	Decomp. temp., °C	Film properties* σ_t, kg cm^{-2}	Film properties* ε, %
$C(CH_3)_2$		270—290	400—420	900	2.6
$C(CH_3)_2$		280—300	430—450	1200	3.0
$C(CH_3)_2$		250—270	395—410	800	3.1
$C(CH_3)_2$		250—260	410—420	1030	3.2
CH_2		260—260	420—430	1150	3.8
CH_2		270—280	410—420	1050	2.5

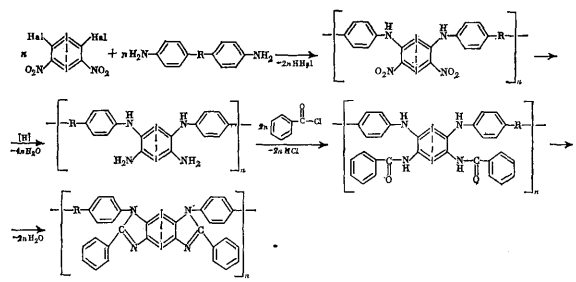
*Film parameters: σ_t = tensile strength; ε = elongation at break.

Thus the reactions represented by scheme (2) are preferred for the synthesis of polyheteroarylenes by reductive polyheterocyclisation. They not only have the disadvantages already mentioned but also somewhat restrict the set of structures obtainable; the nitro-groups have an adverse influence on the reactivity of fragments involved in polycondensation, which is especially marked when bis-*o*-nitroanilines are used as monomers. Processes of modified and combined reductive polyheterocyclisation are in considerable measure free from these defects.

III. MODIFIED AND COMBINED REDUCTIVE POLYHETEROCYCLISATION

Modified reductive polyheterocyclisation differs from the above processes[19–26] in the separation of cyclisation processes by one or more reactions (usually acylation) from nitro–amino reduction stages. As in the previous Section, the modified polymerisation has been conducted as continuous processes in *N*-methylpyrrolid-2-one with reduced iron and hydrogen chloride as reducing agents and the latter as cyclisation catalyst. Since such processes are most complete under homogeneous conditions, attention has been paid mainly to the synthesis of polyheteroarylenes having improved solubility in organic solvents, in particular of phenylated polyheteroarylenes considerably surpassing in solubility the unsubstituted analogues (as has been shown for polybenzimidazoles[50,51], polyquinoxalines[52,53], polyquinazolones[54,55], and several other systems).

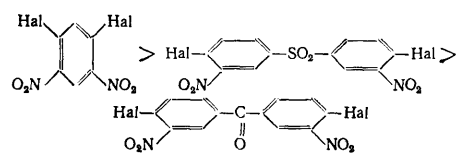
A typical example of modified reductive polyheterocyclisation is the synthesis of hitherto unreported *C*-phenylated polybenzimidazoles[27,28,56–64] by the action of aromatic diamines on activated di-(*o*-halogenonitro)arenes[27,28,56–62], reduction of the resulting poly-*o*-nitro-amines to poly-*o*-amino-amines[27,28,56–60,63], benzoylation of the latter[27,28,56–60,63], and cyclisation of the poly-*o*-benzamido-amines thus formed[27,28,56–60,64]:



(3)

Successful examples of the activated components are 1,3-dihalogeno-4,6-dinitrobenzenes and also dinuclear compounds having electron-accepting bridges[65–71], the 3,3'-dinitro-derivatives of 4,4'-dichloro- and 4,4'-difluorodiphenyl sulphone and -benzophenone; from the above considerations the diamines used have been diphenylmethane-*pp'*-diamine, bis-*p*-aminophenyl ether, and *p*-diphenoxybenzene-*p'p''*-diamine.

A comparative study of the electrophilicity of the di-*o*-halogenonitro-arenes by the application of chlorine-35 nuclear quadrupole and fluorine-19 and carbon-13 nuclear magnetic resonance spectroscopy, and also the results of competitive amination, have shown[60] that the above examples form the reactivity sequence



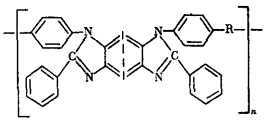
with fluorinated derivatives more reactive than the chlorinated compounds. Although 1,3-dihalogeno-4,6-dinitrobenzenes were the most reactive, attention was paid mainly to polymers from monomers based on diphenyl sulphone and benzophenone, since their "hinge" groups confer solubility in organic solvents on all intermediate and final polymer systems and hence the possibility of effecting synthesis under homogeneous conditions.

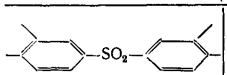
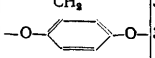
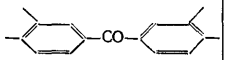
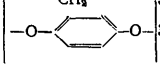
Like the synthesis of polybenzazoles by ordinary reductive polyheterocyclisation, that of *C*-phenylated polybenzimidazoles is an extremely simple process occurring under mild conditions: no stage of the process requires a temperature above 180 °C. The products are free from unreduced nitro-groups and uncyclised fragments (this was established by infrared spectroscopy);[60] their spectral characteristics are completely identical with those of corresponding model compounds.

The mild conditions of cyclisation, the presence of phenyl substituents, and the high content of "hinge" groups in the main chains are responsible for the good solubility of polybenzimidazoles in dipolar, aprotic, and phenolic solvents, while the high viscosity characteristics of these systems (Table 5) make it possible to obtain from them articles that are highly resistant to deformation. Because of the only slight heterounit character[40] the resulting polymers have high degradation temperatures under conditions of dynamic (Table 5) and isothermal thermogravimetric analysis: in

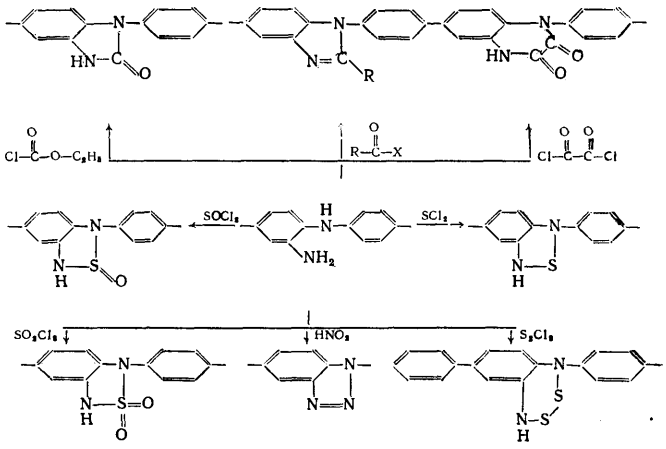
particular, polybenzimidazoles obtained by modified reductive polyheterocyclisation possess greater thermal stability in isothermal thermogravimetry than structurally similar poly-*N*-phenylbenzimidazoles obtained in two stages[50] [Scheme (1) with X = C_6H_5N].

Table 5. Some characteristics of *C*-phenylated polybenzimidazoles of general formula[60]

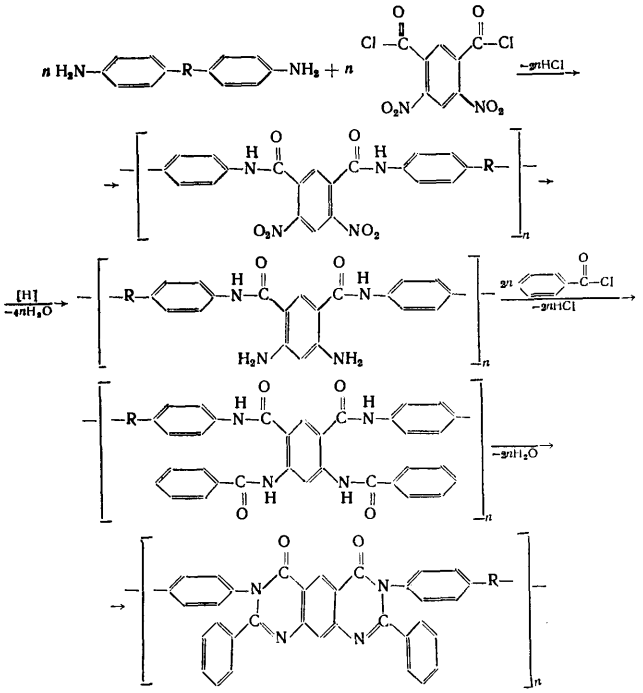


	R	Softening temp., °C	Decomp. temp., °C	Film properties at 25 °C σ_t, kg cm^{-2}	Film properties at 25 °C ε, %
	O	310—330	470	950	4
	CH_2	335—350	490	1040	3—4
		315—330	450	1050	4
	O	305—315	430	—	—
	CH_2	320—325	430	—	—
		300—320	420	990	5

The intermediate poly-o-amino-amides formed in the synthesis of *C*-phenylated polybenzimidazoles can be used to obtain a wide range of heterocyclic polymers[64]. In particular, if they are treated not with benzoyl chloride but with ethyl chlorocarbonate, oxalyl, thionyl, sulphuryl, sulphenyl, and sulphur chlorides, nitric acid, etc., subsequent cyclisation of the reaction products yields polybenzimidazolones, polyquinoxalidinediones, polybenzothiazolidine *S*-oxides, polybenzothiadiazolidine *S*-dioxides, polybenzothiadiazolidines, polybenzodithiadiazines, polybenzotriazoles, etc.:

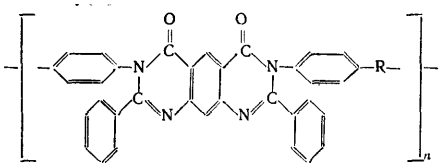


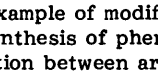
Another typical example of modified reductive polyheterocyclisation is the synthesis of phenylated polyquinazolones[72,73] by reaction between aromatic diamines and 4,6-dinitroisophthaloyl dichloride[74] followed by reduction of the resulting poly-o-nitro-amides to poly-o-amino-amides, benzoylation of the latter at the free amino-groups, and catalytic polycyclisation of the poly-o-benzamido-amines formed:



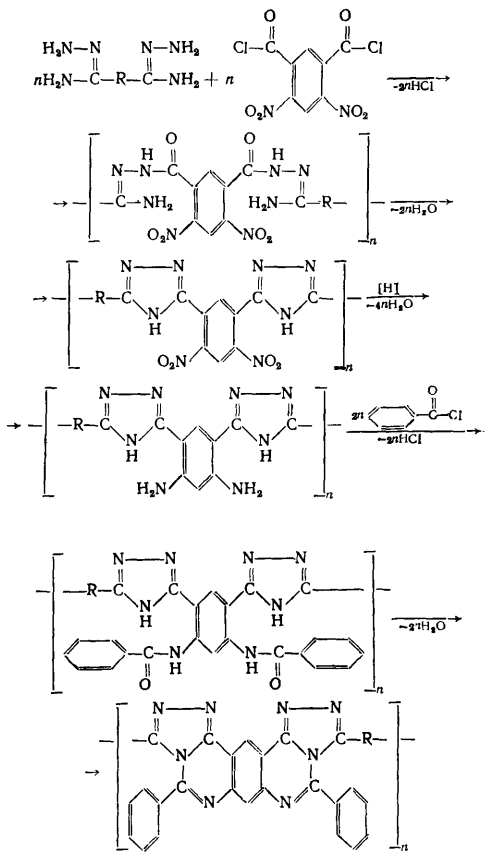
Like *C*-phenylated polybenzimidazoles, poly-2-phenylquinazolones obtained in the same way are free from unreduced nitro-groups and uncyclised fragments, as has been confirmed in particular by the identity of their spectra with those of model compounds[73]. The resulting polymers dissolved in strong acids, in phenolic solvents (Table 6), and on heating in aprotic dipolar solvents. Dynamic and isothermal thermogravimetry indicates that their thermal stability is comparable with that of identical systems obtained by earlier methods[54,55].

Table 6. Some characteristics of poly-2-phenylquinazolones of general formula[72]

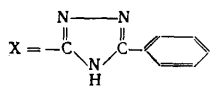


R	Softening temp., °C	Decomp. temp., °C	Film properties at 25 °C σ_t, kg cm^{-2}	Film properties at 25 °C ε, %
O	380—385	450	1200	8
CH_2	375—380	430	1100	8
	350—360	440	1100	12

The enhanced solubility of polyheteroarylenes synthesised by modified reductive polyheterocyclisation made it useful to extend this process to the production of ladder polyheteroarylenes, which are characterised by high heat resistance and thermal stability but unsatisfactory processability into articles[75–77]. With 4,6-dinitroisophthaloyl dichloride and a bisamidrazone of a dicarboxylic acid[78] as comonomers phenylated polybenzodi-sym-triazolopyrimidines were obtained[79,80]:

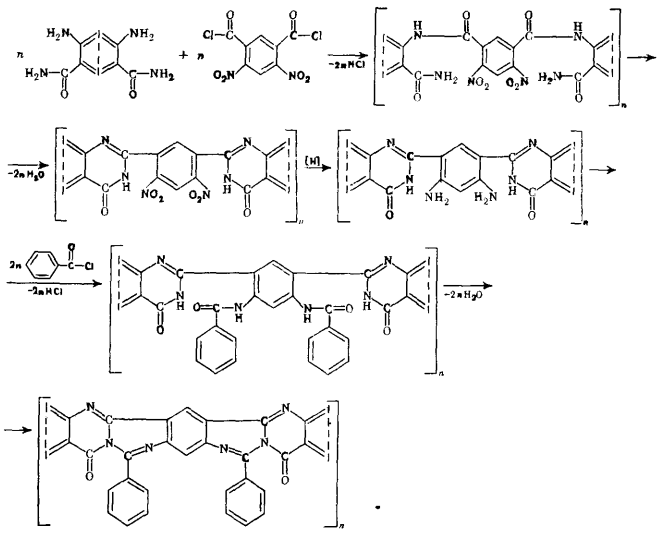


the products being isomeric with previously known systems[81,82] obtained by two-stage processes—scheme (1) with



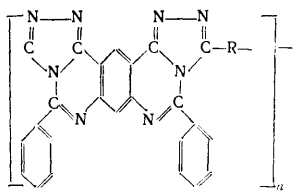
Infrared spectra indicate that polyheteroarylenes obtained in this way are free from unreduced nitro-groups and uncyclised fragments. The presence of phenyl side-groups and the mild conditions of polycyclisation are responsible for the solubility of the resulting systems in acid solvents (sulphuric and trifluoroacetic acids) and a 3:1 tetrachloroethane–phenol mixture, and for their partial solubility in hot *N*-methylpyrrolid-2-one (Table 7). A dynamic (Table 7) and isothermal thermogravimetric study has shown the comparable thermal stabilities of polybenzobis-sym-triazolopyrimidines prepared by modified reductive polyheterocyclisation and by the two-stage method[81,82].

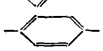
Another example of modified reductive polyheterocyclisation is the synthesis of polyquinazolinoquinazolones[83]:



The resulting polymers are soluble in acids, phenolic solvents, and hot *N*-methylpyrrolidone and dimethyl sulphoxide. Solutions in a 3:1 mixture of tetrachloroethane and phenol have viscosities $\eta = 0.96–1.30$ dl g^{-1}. At 25 °C films based on these polymers possess tensile strengths $\sigma_t = 850–950$ kg cm^{-2} and elongations at break $\varepsilon = 2–10\%$.[38]

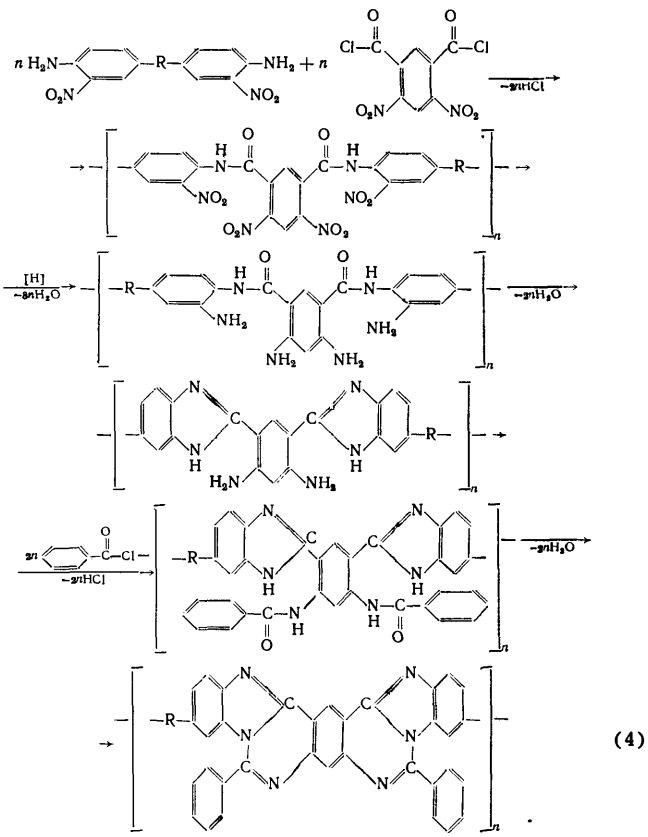
Table 7. Some characteristics of polybenzobis-sym-triazolopyrimidines of general formula[79]



R	Softening temp., °C	Solubility in			
		H_2SO_4	CF_3COOH	$C_2H_2Cl_4 + C_6H_5OH$	MP
—	500	+	+	+	±
	505	+	+	+	+
	520	+	+	+	±
	475	+	+	+	+

Syntheses of ladder polyheteroarylenes have been effected also by combined processes involving true reductive polyheterocyclisation at one stage. A typical example is the synthesis of polybenzodi(pyrimidobenzimidazoles) from

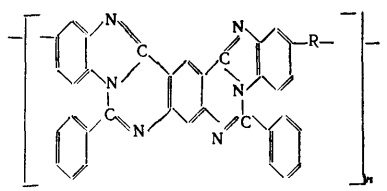
bis-*o*-nitroanilines and 4,6-dinitroisophthaloyl dichloride[84,85]:



(4)

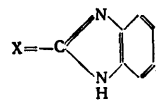
It is evident from (4) that the formation of poly-*o*-aminophenylbenzimidazoles is true reductive polyheterocyclisation, whereas that of the final structure is a modified reductive polyheterocyclisation.

Table 8. Some characteristics of polybenzodi(pyrimidobenzimidazoles) of general formula[84]



R	Softening temp., °C	Solubility in			
		H_2SO_4	CF_3COOH	$C_2H_2Cl_4 + C_6H_5OH$	MP
O	530	+	+	+	±
CH_2	520	+	+	+	±
—O—⟨⟩—O—	500	+	+	+	±

Like all the systems discussed already, polybenzodi(pyrimidobenzimidazoles) obtained by combined reductive polyheterocyclisation are, according to infrared spectral data, free from unreduced nitro-groups and uncyclised fragments. Those obtained by scheme (4) differ from corresponding polymers obtained in two stages[81,82], by scheme (1) with



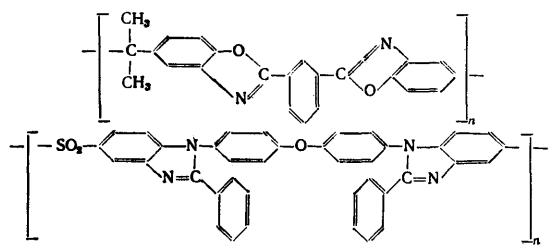
as X, in containing phenyl substituents, which together with the mild conditions of polycyclisation confer solubility in a 3:1 tetrachloroethane–phenol mixture, sulphuric acid, or trifluoroacetic acid (Table 8). Polybenzodi(pyrimidobenzimidazoles) surpass in thermal stability other polyheteroarylenes obtained by modified reductive polyheterocyclisation (Tables 2–8) and are comparable under conditions of isothermal thermogravimetry with polymers obtained in two stages[81,82].

The above syntheses of polyheteroarylenes do not exhaust all the possibilities of modified and combined reductive polyheterocyclisation. Nevertheless, the results surveyed indicate the undoubted promise of such approaches to obtaining comparatively simple and more complicated polymer systems.

IV. CONCLUSION

Thus research during the past five years has developed a new method for synthesising polyheteroarylenes using as intermediates compounds employed in traditional methods. It involves also catalytic cyclisation, with consequent moderation of the reaction conditions and also improvement in the solubility of the resulting systems and their processability into articles.

Among the polymers that have been synthesised the greatest industrial promise is shown by polybenzoxazoles and *C*-phenylated polybenzimidazoles. In particular, those having the structural formula



are of considerable interest. The first system is obtained from 2,2-bis-(4-hydroxy-3-nitrophenyl)propane[86]—a product of the direct nitration of bisphenol A, the latter used in chemical industry to obtain polycarbonates[87] and polysulphones[4]—and isophthaloyl chloride, which finds employment in industry for the production of polyamides[88]. Synthesis of the second system is based on bis-4-chloro-3-nitrophenyl sulphone[89]—formed by the direct nitration of di-p-chlorophenyl sulphone, which is used in industry to obtain polysulphones[4]—and di-p-aminophenyl ether, employed in the manufacture of polyimides[5,6]. The combination in these systems of good solubility with high viscosity characteristics of the polymers makes it possible to obtain from them various materials—films, carbon plastics, gas-separating membranes[22,26,60]—suitable for operation at 250–300 °C. There have been indications

of the practical utilisation of other systems[90] obtained by reductive polyheterocyclisation.

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Oligomeric Alkoxyphosphazens

V.V.Kireev, V.I.Astrina, and E.A.Chernyshev

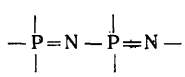
Methods of preparation, properties, and applications of oligomeric linear, cyclic, and cyclolinear alkoxy- and aryloxyphosphazens are surveyed. General syntheses of various types are suggested. A list of 164 references is included.

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I. INTRODUCTION

The chemistry of oligomeric linear and cyclic phosphazens owes its intense development to the specific properties of this group of compounds, which are inorganic in nature but possess many of the properties of organic compounds. One of the chief problems in the chemistry of cyclotriphosphazens is to determine the nature and the character of the delocalisation of π electrons in the cyclic molecules. An important aspect of linear phosphazens is the character of the conjugation of double bonds in

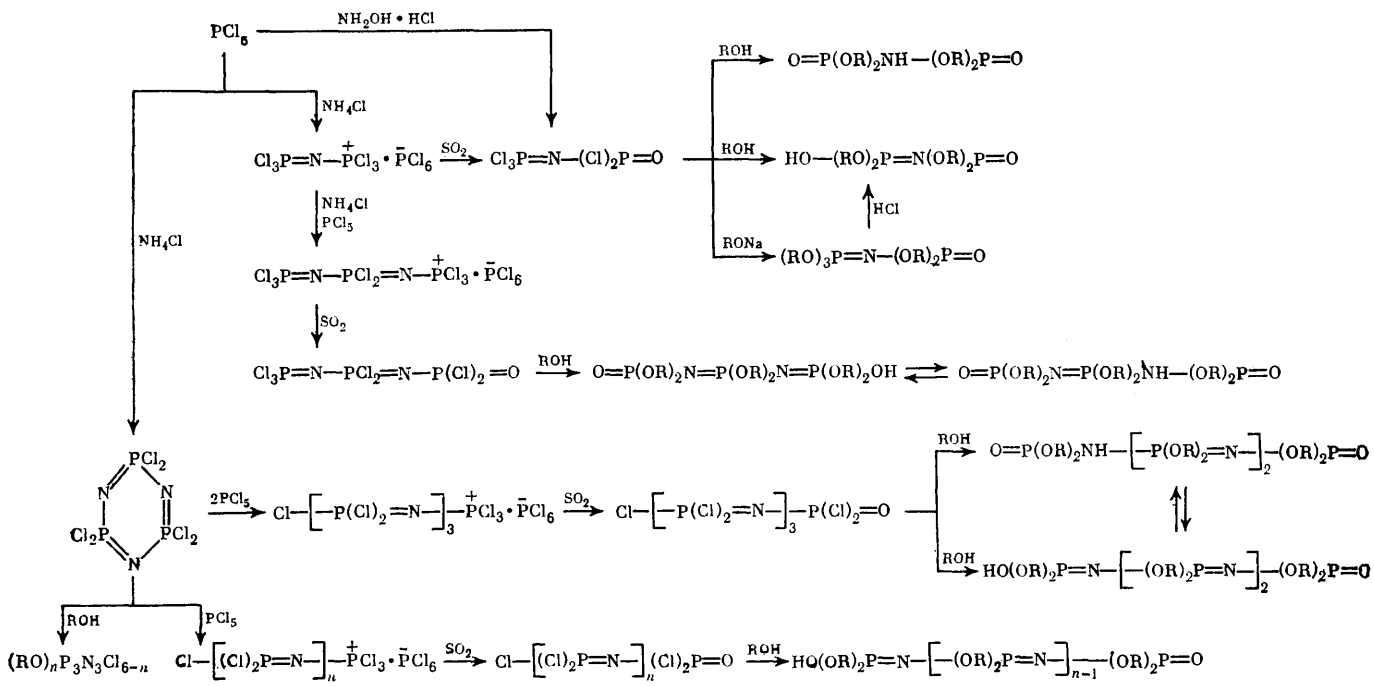


systems and its influence on the chemical properties of various derivatives.

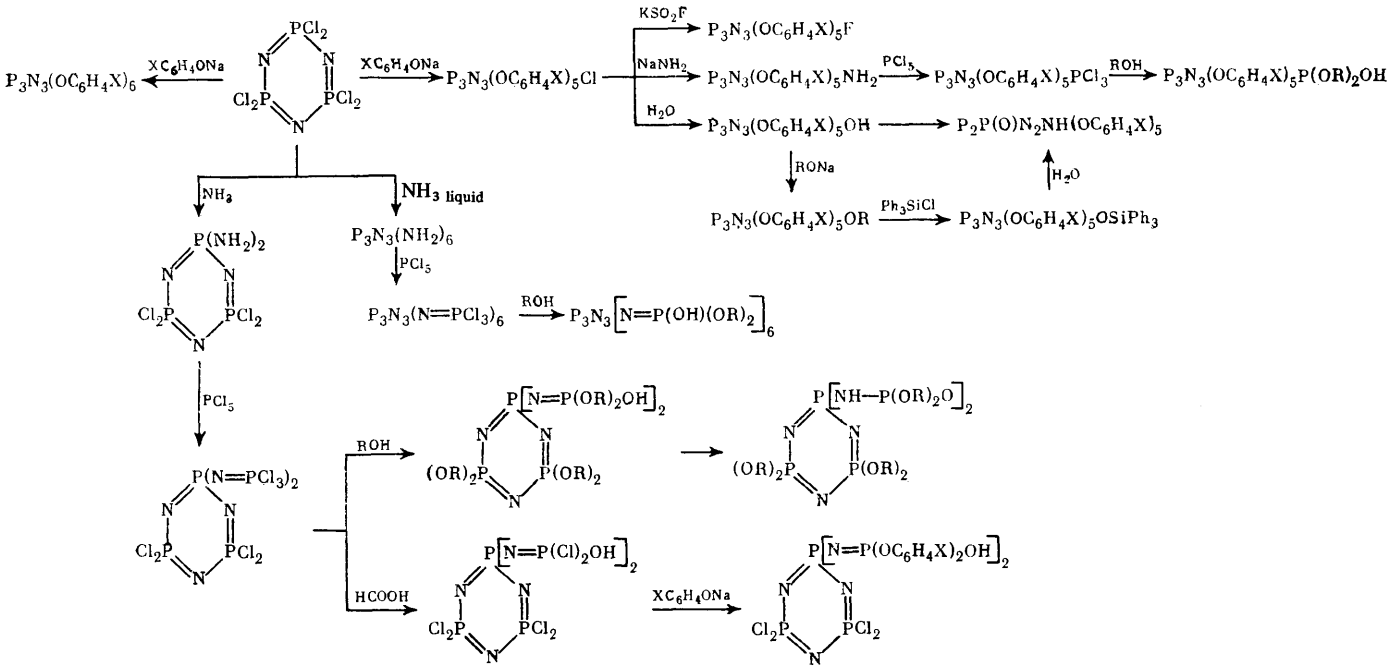
Because of the hydrolytic instability of most halogenophosphazens the most accessible and convenient compounds for investigation are linear and cyclic alkoxyphosphazens, which are formed by treating the corresponding halogenated compounds with alcohols, phenols, alkoxides, and phenoxides. Besides their scientific interest alkoxyphosphazens have recently acquired great practical value: they are finding increasing application as starting materials in the synthesis of polymers, chemically resistant and thermally stable oligomeric liquids for various purposes (hydraulic and lubricating oils, heat-transfer agents, plasticisers, complexing agents, etc.).

Individual aspects of the chemistry and application of alkoxyphosphazens have been partly surveyed[1-9]. During recent years much new information has accumulated in this field and additional interesting results have been obtained.

Scheme 1.



Scheme 2.



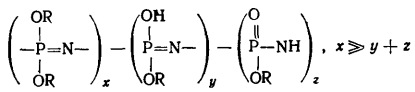
Our aim is to summarise recent advances in the synthesis, structure, properties, and application of oligomeric alkoxyphosphazens.

II. METHODS OF SYNTHESIS

Synthetic routes to oligomeric linear alkoxyphosphazens are summarised in Scheme 1, and those to the cyclic and cyclolinear oligomers in Scheme 2.

1. Linear Alkoxyphosphazens

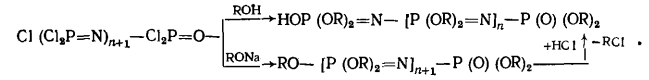
Because of the great activity of the chlorine atoms in linear chlorophosphazens they begin to react with alcohols even at room temperature. The resulting mixture of homologues contains not only acidic alkoxyphosphazens but also decomposition products of chlorophosphazens extending to polyphosphinic acids. Thus alcoholysis with higher alcohols of a mixture of linear chlorophosphazens of mean degree of polymerisation 10—11 gives a mixture of products to which the formula



has been assigned[10].

The first individual linear phosphazens—dialkyl trialkoxyphosphazophosphates of general formula $(RO)_3P{:}N.PO(OR')_2$—have been synthesised by reaction between a trialkyl phosphite and dibutyl azidophosphate[11-13] or between an alkoxide and trichlorophosphazophosphonyl dichloride. Under the influence of hydrogen chloride these compounds readily eliminate an alkyl chloride and are converted into tetra-alkyl imidobisphosphates[11,12].

Imidobisphosphoric esters can be obtained by alcoholysis of trichlorophosphazophosphonyl dichloride with alcohols in the presence of a tertiary amine[14]. Homologues of general formula $HO.[P(OR)_2{:}N]_n.PO(OR')_2$ have also been synthesised from linear chlorophosphazens[15]. The series begins with tetra-alkyl imidobisphosphates:



Alcoholysis of the chlorophosphazophosphonyl dichloride was conducted in benzene or oxolan in the presence of triethylamine at temperatures from −5 to 0 °C. Rise in temperature causes partial depolymerisation, and also formation of P—O—P bonds.

Compounds prepared in the course of the investigations were alkyl imidobisphosphates ($n = 0$), dialkoxyphosphoriobisamidophosphates ($n = 1$), and nitridobisdialkoxophosphorioamidophosphates ($n = 2$), as well as oligomeric alkoxyphosphazens ($n > 5$). All these compounds are present as two tautomeric forms[12]—phosphazen and phosphazan:

$$-N{=}P(OR)_2OH \rightleftarrows -NH-P(O)(OR)_2,$$

which is confirmed by infrared and nuclear magnetic resonance spectroscopy.

2. Cyclic Alkoxyphosphazens

Tris- and tetrakis-phosphonitridic esters can be obtained by the action of hexachlorocyclotriphosphazen and of octachlorocyclotetraphosphazen on almost all stable alcohols and phenols (acceptor method) or even by the use of sodium alkoxides and phenoxides as nucleophiles (alkoxide method). In the former case a tertiary organic amine, such as

triethylamine or pyridine, or sodium carbonate must be added to remove the hydrogen halide that is formed[16-19].

For reactions of this type use can be made of various anhydrous solvents[4,20-26]—diethyl ether, oxolan, dioxan, benzene, toluene, xylene, acetone, butan-2-one, dimethylformamide, perfluoro-t-butylamine, pyridine, and also excess of the alcohol employed as substituting reagent—choice between which must take into account polarity and also ability to dissolve sodium alkoxides and phenoxides. Potentiometric titration has established[27] that the initial rate of reaction between hexachlorocyclotriphosphazen and sodium methoxide is considerably greater in dimethylformamide than in acetone, dioxan, butanol, and mixtures of dioxan with acetone and with butan-2-one. The rate of substitution decreases in the sequence of solvents—dimethylformamide at 100 °C ≫ boiling diglyme > boiling oxolan > boiling benzene > boiling diethyl ether[4].

(*a*) Completely substituted alkoxyphosphazens

The first individual hexamethoxy- and hexabutoxy-cyclotriphosphazens were obtained by the action of the alcohols on hexachlorocyclotriphosphazen in the presence of pyridine[28]. Hexaethoxycyclotriphosphazen was isolated by the action of sodium ethoxide in ethanol[29]. Hexapropoxyphosphazen was obtained in 94% yield by the action of sodium propoxide in heptane or octane[30,31]. Unusual alkoxy-derivatives have been obtained by reaction between sodium salts of cellulose and hexachlorocyclotriphosphazen in dioxan[32]; the activation energy is 35.6 kJ mole^{-1}.

A detailed investigation of the alcoholysis of hexachlorocyclotriphosphazen and octachlorocyclotetraphosphazen was undertaken by Shaw and his coworkers[33], who used the acceptor method to synthesise trimeric and tetrameric compounds by the action of ethyl, propyl, and butyl alcohols, and the alkoxide method for methyl and isopropyl alcohols, phenol, *p*-methoxyphenol, and 2-naphthol. The former method was more convenient with respect to preparation (it did not require synthesis of the alkoxide), but could not be applied in all cases. Hexamethoxycyclotriphosphazen can be obtained only via the methoxide, since the ether formed decomposes when the excess alcohol and the pyridine are distilled off. Secondary and higher alcohols react with greater difficulty, and here it is more convenient to use the alkoxide method[4].

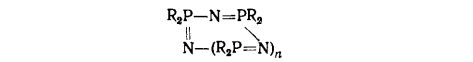
(*b*) Partly substituted alkoxycyclophosphazens

Partly substituted alkoxycyclophosphazens have little thermal stability. Allyloxy- and propoxy-pentachlorocyclotriphosphazens have been obtained[34], as well as mono-, di-, tri-, tetra-, and penta-butyl ethers of hexachlorocyclotriphosphazen[26] by means of sodium butoxide in methanol. The hexachloro-phosphazen hardly reacts at all with butanol at 20 °C.[35] In the presence of pyridine under the same conditions only 50% reaction (based on substitution of one chlorine atom) has taken place after 3 h. Replacement of the first three chlorine atoms takes place non-geminally[35]. The rate drops sharply as chlorine atoms are substituted by alkoxy-groups[36].

Partly (geminally and non-geminally) alkoxylated phosphazens have been studied by mass spectrometry and by hydrogen-1 and phosphorus-31 nuclear magnetic resonance spectroscopy[37,38].

Methylaminopentapropoxycyclotriphosphazen has been obtained by reaction of hexachlorocyclotriphosphazen with sodium propoxide and with methylamine[39].

Chloroalkoxyphosphazens of general formula



$R=OCH_2CHClR'$, $R'=H$, Me, $ClCH_2$, Ph, $n \geqslant 1$

can be obtained by the action of oxirans



on hexachlorocyclotriphosphazen in the presence of aluminium trichloride[40].

(*c*) Alkoxyphosphazens with various substituents in aliphatic radicals

Mixed cyclophosphazens of general formula $N_4P_4(C_6H_5)_4 \cdot (OR)_4$, where R = CH_3, C_2H_5, C_6H_5, containing not only alkoxyl but also phenyl groups, have been prepared by alcoholysis of three geometrical isomers of tetrachlorotetraphenylcyclotetraphosphazen[41].

The action of equimolecular quantities of sodium *m*-fluorophenoxide and trifluoroethoxide on hexachlorocyclotriphosphazen gave a product containing aryloxy- and trifluoroethoxy-groups[42], but the positions of the substituents were not established. The end-product of the action of sodium phenoxide on the hexachloro-phosphazen in butanol contained both phenoxy- and butoxy-groups[26], but their relative contents were not given.

The alcoholysis of bis- and tris-dimethylaminocyclotriphosphazens and of tetrachlorodiphenylcyclotriphosphazen was studied[43], but the products were not separated into geometric isomers.

In the production of new pesticides by treating 2-monoalkylamido-6-chloro-2,4,4,6-tetrakis-*N*-dimethylamidocyclotriphosphazen with alkoxides of various alcohols derivatives of hexachlorocyclotriphosphazen containing one alkoxy-group and five *N*-substituted amino-groups were obtained[44].

(*d*) Fluorinated alkoxyphosphazens

The first fluorine-containing alkoxyphosphazens obtained[45] had the general formula $[NP(OCY_2[CF_2]_nCF_2X)_2]_m$ where Y = H, Cl; X = F, H; m = 3, 4; n = 0, 2 (when X = F) and n = 1, 3, 5, 7, 9 (when X = H).

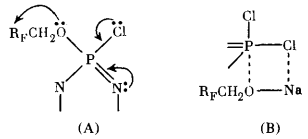
In a combined study of the action of sodium trifluoroethoxide on hexachlorocyclotriphosphazen[46] compounds of general formula $N_3P_3Cl_{6-n}(OCH_2CF_3)_n$ were obtained with n = 1, 2 (two isomers), 3 (three), 4 (two), 5, or 6. Nuclear magnetic resonance spectroscopy was used to study the structure of derivatives having n = 2–4. The formation of predominantly *trans*-non-geminal isomers was attributed[46] to steric hindrance.

Chlorination of heptafluorobutyl heptafluoropropyl amidophosphonite followed by dehydrochlorination of the resulting aminodichlorophosphorane gave[47] a mixture of hitherto unknown trimeric and tetrameric heptafluorobutoxy-derivatives $[XCH_2OPNX]_n$, where X = C_3F_7 and n = 3 or 4.

Reaction of 2,4,6,6-tetrachloro-*trans*-2,4-bisdimethylaminocyclotriphosphazen with sodium trifluoroethoxide CF_3CH_2ONa yielded[48] products in which 2–4 chlorine atoms had been replaced by trifluoroethoxy-groups: the two chlorine atoms attached to the same phosphorus atom were replaced first, and then one *geminal* to a dimethylamino-group. In the series of compounds $N_3P_3H_nCl_{6-n}OCH_2CF_2 \cdot CF_3$ (n = 1–6) a non-geminal chlorine atom has a tendency to adopt a *trans*-configuration[49]. Compounds in which

n = 2–6 exist as an equilibrium mixture of several conformers.

In an investigation of the reaction of hexachlorocyclotriphosphazen with fluorinated sodium alkoxides $NaOR_F$, where R_F = $CH_2CF_2CF_2H$, $CH_2[CF_2]_3CF_2H$, $CH_2[CF_2]_5CF_2H$, a complete series of products $N_3P_3Cl_{6-n}(OR_F)_n$ (n = 1–6 and R_F = $CH_2CF_2CF_2H$) was isolated by gas–liquid chromatography[50]. It has been shown by ^{31}P n.m.r. spectroscopy that in the case of compounds having n = 2–4, as when R_F = CH_2CF_3,[46] mainly non-geminal isomers are formed[51]. The predominantly non-geminal character of the substitution of chlorine by the action of sodium and lithium fluoroalkoxides on hexachlorocyclotriphosphazen was explained[51] in terms of a four-centre transition complex. With a fluoroethoxy-group already attached the phosphorus–chlorine bond can be strengthened by p_π–d_π interaction; when neither chlorine atom has been replaced, the phosphorus–chlorine bond is readily polarised and capable of forming a transition complex of type (B):



(A) (B)

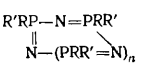
Examination of the infrared spectra of mixtures of fluorinated cyclophosphazens of types $N_3P_3(OCH_2R_F)_6$ and $N_3P_3Cl_3(OCH_2R_F)_3$, where R_F = C_2F_4H, C_2F_5, C_3F_7, revealed an enhancement of basicity on the replacement of chlorine by fluoroalkoxy-groups[52]. The aggregate inductive and resonance effects of the groups apparently increase the electron density on the phosphorus atom relative to the effect of chlorine, and the weakening of p_π–d_π interaction in the ring enhances the basicity of the nitrogen atom.

(*e*) Aryloxycyclophosphazens

Aryloxycyclophosphazens have attracted the attention of investigators by virtue of their specific properties, especially their thermal and chemical stability.

Phenoxy- and *p*-bromophenoxy-cyclotriphosphazens of all degrees of substitutions are now known[22]. The action of sodium and potassium phenoxides and *p*-bromophenoxides on hexachlorocyclotriphosphazen follows a non-geminal pattern in benzene, acetone, and oxolan[22,24,53,54]. In acetone *cis* substitution predominates over *trans*, which was discovered by displacing the remaining chlorine atoms by dimethylamino- and amino-groups[53] and analysing the high-resolution ^1H n.m.r. spectra. Reaction between 2,2-diphenyltetrachlorocyclotriphosphazen and sodium phenoxide involves non-geminal substitution of two chlorine atoms and formation of three-dimensional *cis–trans* isomers[23].

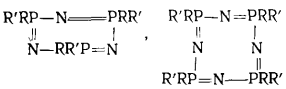
Halogenophenoxyphosphazens, used as flame-retardant additives in polyesters, have been obtained[55] by treating with sodium propoxide the reaction product from hexachlorocyclotriphosphazen and a halogenophenol. This process gave bromoarylphosphazens of general formula



in which R represents *p*-bromophenoxy, 2,4,6-tribromophenoxy, pentabromophenoxy, 2,4,6-tribromo-3-methylphenoxy, 1,4-dibromo-2-naphthyloxy; R' is either chloro or *p*-bromophenoxy; and $n \geq 1$.[56]

The action of *p*-nitrophenoxides on hexachlorocyclotriphosphazen and on octachlorocyclotetraphosphazen gives products of various degrees of substitution (other than 2 and 4). Replacement of the first three chlorine atoms (in the former compound) takes place non-geminally. Even in the presence of two geminal phenyl substituents phenolysis gives predominantly non-geminal compounds[57]. As with fluoroalkoxy-derivatives, this is due to the geometrical dimensions of the nucleophile[4]: bulky side-groups are most difficult to introduce as substituents in the phosphazen ring.

The action of sodium aryloxides on the above chlorocyclophosphazens on heating in a solvent gives aryloxy-derivatives of general formula $[NP(OAr)_2]_n$ (where with n = 3, Ar = *p*-ClC_6H_4, *p*-FC_6H_4, C_6F_5; and with n = 4, *p*-FC_6H_4, C_6F_5) [58] and also derivatives of the type



in which R = C_6H_5O, $CH_3C_6H_4O$ (*o*, *m*, *p*), 2-$C_{10}H_7O$ and R' = Cl or R.[59]

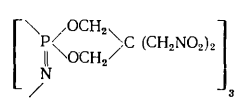
Aryloxyphosphazens containing various functional groups have been synthesised by reduction of nitrophenoxyphosphazens[25] followed by phosgenation[60] and also by hydroxyalkylation of aryloxyphosphazenamines[61]. The action of glycols on phenylchlorocyclophosphazens gives phenylcyclophosphazenoxyalkanols $P_nN_n(C_6H_5)_n(OROH)_n$, with R = $[CH_2]_2$, $[CH_2]_4$ and n = 3, 4.[62]

Completely substituted aryloxyphosphazens, containing either the same or different aryloxy-groups (phenoxy, *m*-trifluoromethoxyphenoxy) are produced[63,64] e.g. by boiling in xylene a mixture of potassium hydroxide, hexachlorocyclotriphosphazen, and *m*-trifluoromethoxyphenol and removing the water formed. Compounds of general formula $ROP_3N_3(OC_6H_5)_5$, in which R = *m*- or *p*-$C_6H_5OC_6H_4$, have been obtained[65]. Treatment of the chlorocyclophosphazen with phenoxides in oxolan yields a series of aryloxycyclotriphosphazens of general formula $(XC_6H_4O)_6P_3N_3$, where X = Cl, F, NH_2, AlkO, HO.

Aryloxy-derivatives *p*-$RC_6H_4ON_3P_3Cl_5$ (R = H, F, Cl, CH_3, CH_3O) have been obtained by reaction with the corresponding sodium aryloxides[66]. The trifluoroethoxide anion $CF_3CH_2O^-$ is able to replace aryloxy-groups[67], e.g. in $N_3P_3(OAr)_6$ to give a series of products $N_3P_3(OCH_2CF_3)_n(OAr)_{6-n}$, where Ar = *p*-$NO_2C_6H_4$ and n = 1–5. Ease of substitution diminishes in the Ar sequence *o*-, *p*-$NO_2C_6H_4$ > *p*-ClC_6H_4 ≥ C_6H_5.

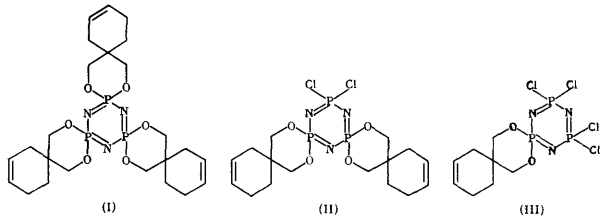
3. Spiroalkoxycyclophosphazens

Spirocyclic compounds are of interest as intermediates in the synthesis of polymers[4]. Among the first to be isolated were[68,69]



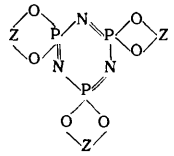
and also 2,2,4,4-tetrachloro-6,6-ethylenedioxycyclotriphosphazen[34]. Spiroalkoxycyclophosphazens have been obtained also by reaction of hexachlorocyclotriphosphazen and of octachlorocyclotetraphosphazen with glycols[70,71], hydroxyalkoxides[72], pyrocatechol[16,18,70,73], and *ortho*- or *ortho-ortho'*-substituted dihydroxynaphthalenes[74]. The tetrameric cyclic analogue is exceptionally unstable and difficult to isolate[4].

Several spiro-derivatives have been synthesised by treating hexachlorocyclotriphosphazen with sodium or triethylamine salts of fluoroglycols[45,51], 1″-hydroxy-2,2-dimethylpropane-1,1′-diyl-3-ylidyne pentanitrate[68], propane-1,2-diol, and cyclohexane-1,2-diol.[69] Reaction of the chlorocyclophosphazen with 4,4-bishydroxymethylcyclohexene yields[75] the completely and partly substituted spiro-compounds



(I) (II) (III)

Compound (I) can be obtained also from chloro-*o*-phenylenedioxyphosphine and trimethylsilyl azide[76]. With an aromatic diol and pyrocatechol compounds of type



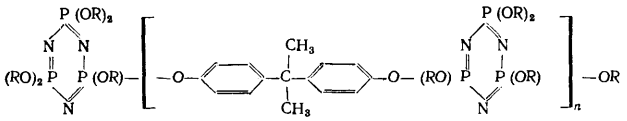
are formed, where Z = *o*-C_6H_4, 2,3- or 1,8-$C_{10}H_6$.[77]

4. Cyclolinear Alkoxyphosphazens

Mixed phosphazens, containing linear phosphazo-groups as well as cyclic units, are extremely interesting, having conjugation between exocyclic phosphazo-groups and the phosphazen ring, as well as other interactions, and also the possibility of combining in a single compound the specific properties of cyclic and linear phosphazens.

Mixed alkoxyphosphazens of general formula $(RO)_{6-n}P_3N_3 \cdot [N{:}P(OR')_2OH]_n$ (where R, R′ = Alk, Ar, and n = 1, 2, 6) have been prepared[78,79] via the corresponding amino-chlorocyclophosphazens by Kirsanov's reaction followed by the replacement of chlorine by alcohol or phenol residues. Cyclophosphazens containing a single exocyclic phosphazo-group have been obtained via penta-aryloxychlorocyclophosphazens. Intermediate cyclolinear chlorophosphazens are hydrolytically unstable, and have not been isolated in pure form.

The action of phenol or a halogenophenol, bisphenol A, 4,4-dihydroxydiphenols, resourcinol on hexachlorocyclotriphosphazen gives an oligomeric product



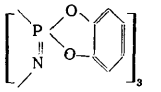
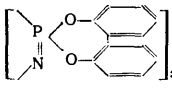
used as flame-retardant additive in the production of polyester fibres[80,81].

III. PHYSICAL PROPERTIES

The majority of completely substituted alkoxy- and aryloxy-phosphazens are stable white crystals readily soluble in organic solvents, with the exception of spirocyclic compounds, which dissolve with difficulty in polar solvents. All the cyclolinear phosphazens that have been prepared and investigated are viscous liquids. Several alkoxyphosphazens, e.g. $[NP(OC_2H_5)_2]_3$, $[NP(OC_4H_9\text{-}n)_2]_3$, $[NP(OCH_3)_2]_{5,7}$, are colourless oily liquids at room temperature[82]. Substitution of fluoroalkoxy- or aryloxy-groups for halogen atoms in the trimeric or tetrameric ring lowers the melting point considerably[42,83].

In the infrared spectra of alkoxy- and aryloxy-cyclotriphosphazens the bands corresponding to vibrations of the trimeric and tetrameric rings are displaced in some measure to shorter wavelengths[84,85] relative to the initial chlorophosphazens (1218 and 1300 cm^{-1}). Table 1 gives several structural data obtained for alkoxyphosphazens by X-ray diffraction and by ultraviolet, infrared, and nuclear magnetic and nuclear quadrupole resonance spectroscopy.

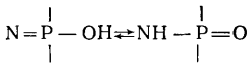
Table 1. Bond angles and lengths in some alkoxyphosphazens.

Compound	Bond lengths, Å		Bond angles, °				Ring or chain structure	Ref.
	P—N	P—O	N—P—N	P—N—P	P—O—C	O—P—O		
$[NP(OC_6H_5)_2]_3$	1.58	—	117.3	121.9	94.1	—	slightly buckled ring	[86]
$[NP(OCH_3)_2]_4$	1.58	—	122	132	105	—	buckled ring (saddle)	[87]
$[NP(OCH_3)_2]_6$	1.56	1.58	116.7	136.7	101.3	—	buckled ring	[88]
	1.58	1.59	117.5	122.5	109	97	—	[89]
	1.57	1.58	118.4	121.0	—	120.7	—	[90]

Study of the structure of spirocyclic compounds showed[89] that on formation of a five-membered cyclic system ∠OPO = 97°. Such a decrease in angle (relative to cyclophosphazens, in which ∠RPR ≈ 100° [4]) is due to the constricting influence of the five-membered ring. For a seven-membered exocyclic system[91] ∠OPO = 102.5°, the stress being diminished by rotation of the side-group. In trisdibenzodioxaphosphepinspirocyclotriphosphazen[90] two dibenzodioxaphosphepin units are each rotated successively through 43° in one direction, but the third is rotated through 52° in the opposite direction. The infrared and Raman spectra indicate that alkoxy-groups (fluoroalkoxy, phenoxy, methoxy, ethoxy, n-propoxy, n-butoxy) increase the strength of a skeletal bond[18,33,92,93].

Alkoxyphosphazens are intermediate between chloro- and amino-cyclophosphazens with respect to the basicity of the ring nitrogen atoms[94], which is weakened by electron-accepting substituents, but strengthened by electron-donor groups. In conformity with the variation of the inductive effects of the substituents the basicity of trimeric and tetrameric alkoxy- and aryloxy-phosphazens diminishes in the sequence isopropoxy > ethoxy ≈ n-butoxy > methoxy > benzyloxy > *p*-methoxyphenoxy > phenoxy > trifluoroethoxy, 2-naphthyloxy[94]. In general tetrameric alkoxyphosphazens are more basic than the corresponding trimeric compounds (where R = CH_3O, C_2H_5O, $(CH_3)_2CH.O$, n-C_4H_9O, $C_6H_5CH_2O$, *p*-$CH_3OC_6H_4O$). However, hexaphenoxycyclotriphosphazen is more basic than octaphenoxycyclotetraphosphazen[95].

Linear, cyclic, and cyclolinear alkoxyphosphazens containing P.OH groups are characterised by the amide–imide equilibrium



(a particular case of the phosphazen–phosphazan rearrangement), the position of which shifts according to the structure and nature of the substituting groups (Tables 2–4).

Table 2. Ionisation constants and position of amide–imide equilibrium for linear alkoxyphosphazens.

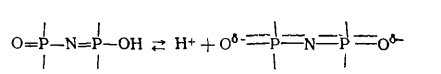
$O{=}P(OR)_2NH{-}[(OR)_2P{=}N]_{n-1}{-}(OR)_2P{=}O \rightleftarrows$
(Am)
$\rightleftarrows HO{-}[(OR)_2P{=}N]_n{-}(OR)_2P{=}O$
(Im)

R	n	pK_a	Amide / Imide
C_4H_9	1	6.0	35:65
$H(CF_2)_2CH_2$	1	6.0	70:30
$H(CF_2)_4CH_2$	1	6.4	65:35
C_4H_9	2	7.2	(Am) < (Im)
iso-C_8H_{17}	2	7.3	(Am) < (Im)
C_4H_9	3	7.6	(Am) < (Im)
iso-C_8H_{17}	3	7.6	(Am) < (Im)

Table 3. Constants and position of amide–imide equilibrium for cyclic alkoxyphosphazens $P_3N_3(OH)_n(OR)_{6-n}$ and cyclolinear alkoxyphosphazens $(RO)_{6-n}P_3N_3[N{:}P(OR')_2OH]_n$.

R	R′	n	pK_a	Amide / Imide
cyclic alkoxyphosphazens				
C_6H_5	—	1	8.3	(Am)
p-$CH_3C_6H_4$	—	1	8.6	(Am)
$(C_2H_5)_2CHCH_2$	—	2	10.0	(Am)
$(CH_3)_2CHCH_2$	—	3	10.0	(Am)
iso-C_8H_{17}	—	2	10.1	(Am)
iso-C_8H_{17}	—	3	10.1	(Am)
cyclolinear alkoxyphosphazens				
C_6H_5	C_6H_5	1	10.4	(Im) > (Am)
C_6H_5	$C_2H_4OCH_3$	1	10.2	(Im) > (Am)
p-$CH_3C_6H_4$	n-C_4H_9	1	10.4	(Im) > (Am)
p-$CH_3OC_6H_4$	n-C_4H_9	1	10.4	(Im) > (Am)
C_6H_5	C_6H_5	2	9.1	(Am) > (Im)
p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	2	9.2	(Am) > (Im)
o-$C_6H_5C_6H_4$	o-$C_6H_5C_6H_4$	2	8.9	(Am) > (Im)
o-BrC_6H_4	o-BrC_6H_4	2	8.7	(Am) > (Im)
o-ClC_6H_4	o-ClC_6H_4	2	8.7	(Am) > (Im)
m-$CH_3C_6H_4$	m-$CH_3C_6H_4$	2	9.2	(Am) > (Im)

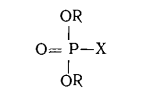
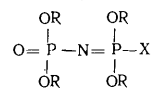
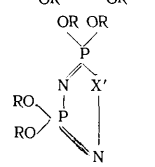
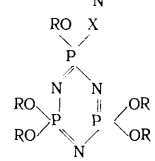
Linear alkoxylated hydroxyphosphazophosphinoyl derivatives are monobasic acids, which become weaker with increase in the number of phosphazo-groups. This is due to conjugation, which facilitates dissociation of the groups



and diminishes with increase in length of the phosphazen chain[96]. It is for this reason that the pK_a value changes so substantially on passing from mono- to di-phosphazophosphinoyl esters—from 6.0 to 7.2 (Tables 2 and 4). The nature of the organic groups has hardly an influence on the pK_a value, but affects the position of equilibrium significantly. When alkyl radicals are replaced by perfluoroalkyl, which are strong electron acceptors, the values for the phosphazo-compounds remain almost unchanged, but the amide–imide equilibrium is displaced towards the amide form.

The nature of the terminal atom attached to a phosphorus atom has an appreciable influence on the acidity of short phosphazen chains, an effect which diminishes sharply with increase in the number of phosphazo-groups. In cyclic compounds the amide–imide equilibrium is displaced towards the amide form[97]. Comparison of the ionisation constants (Table 3) indicates that the pK_a increases with the electron-donor properties of the radicals. Cyclic alkoxy-hydroxy-phosphazens are considerably less strongly acidic than short-chain linear analogues, owing to absence of the complete delocalisation of electrons in the ring that is characteristic of aromatic systems, and the consequent absence of conjugation.

Table 4. Ionisation constants and position of amide–imide equilibrium of alkoxyphosphazens.

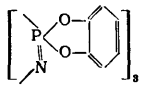
Compound*	R	pK_a**	Amide / Imide
	Alk	6.0—7.0	(Am) + (Im)
	Alk	7.0—9.0	(Am) + (Im)
	Ar	8.5—10.0	(Am)
	Ar	8.8—9.3	(Am) > (Im)
	Alk	10.7—11.4	(Im) > (Am)

*X = $HOP(OR)_2{:}N-$; X′ = $-P(OH)(OR){:}N-$. Different arrangements of the fragments X and X′ in the phosphazen molecules govern the value of pK_a.

**In ethanol at 25 °C.

Tables 3 and 4 illustrate the influence of the nature of organic substituents in exocyclic phosphazo-groups on the position of the amide–imide equilibrium. The amide form predominates in aryloxy-derivatives, and the imide form in the alkoxy-compounds. With the same number of exocyclic phosphazo-groups displacement of the equilibrium to one side or the other is determined by the nature of the alkoxy-group[98]. Cyclolinear alkoxyphosphazens are characterised by sharply diminished acidity in comparison with imidobisphosphoric esters (Tables 2–4). This confirms the absence of conjugation between exocyclic phosphazo-groups and the cyclotriphosphazen ring, and also supports the hypothesis[99] that π-electrons are not completely delocalised in this cyclic system.

Aryloxylated spiro-compounds containing a five-membered exocyclic system are able to form inclusion compounds with various organic solvents[100]. Thus tribenzodioxaphospholespirocyclotriphosphazen absorbs the vapours of many organic solvents (other than methanol, triethylamine, pyridine, and acetic acid). X-Ray diffraction indicates that the process is accompanied by a change in crystal structure from triclinic or monoclinic for the pure compound to hexagonal for the adduct, with the lattice containing one solvent molecule per two spirophosphazen molecules. Allcock[4] links inclusion with the dimensions of the side-groups and the deformability of the crystal lattice. Such an interpretation suggests that related cyclophosphazens containing bulky side-groups should behave similarly. The molecular structure of



has been determined by X-ray diffraction[101]: the P—N bond length is 1.59 Å, and the PNP angle is 122°; the position of benzene in the clathrate has not been determined accurately owing to the effect of rotation.

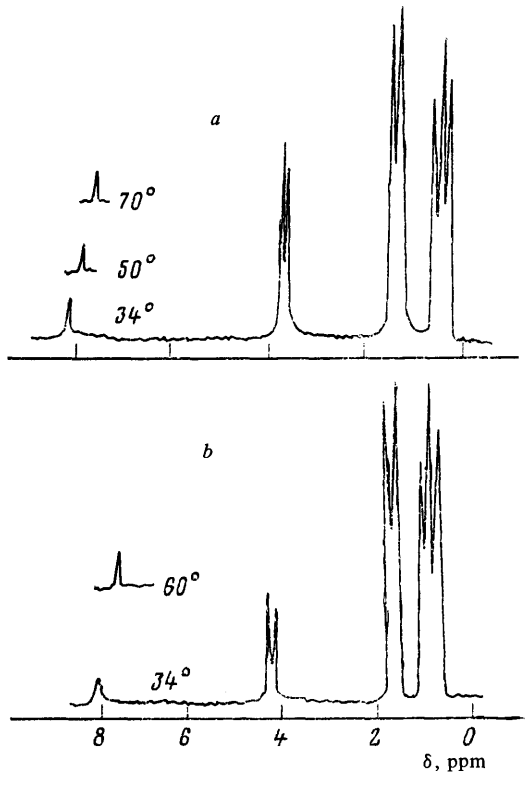


Figure 1. Spectra (^{1}H n.m.r.) [14] of: *a*) dibutyl hydrogen dibutoxyphosphinoylimidophosphate; *b*) bis-2-ethylhexyl hydrogen bis-2′-ethylhexyloxyphosphinoylimidophosphate.

Nuclear magnetic resonance spectroscopy has been used to establish the structure of many alkoxyphosphazens[14,102–106]. The proton chemical shifts δ are sufficiently characteristic of various groups. The ^{1}H n.m.r. spectra of linear alkoxyphosphazens confirm the presence of amide–imide equilibrium. Thus in the spectrum of dibutyl hydrogen dibutoxyphosphinoylimidophosphate (Fig.1*a*) signals corresponding to CH_3, CH_2, and CH_2O groups (0.95, 1.4, and 3.7–4.0 ppm) are accompanied by a signal having δ = 8.2 ppm (at 34 °C), which corresponds to the hydroxyl proton. On heating to 50 and 70 °C this signal shifts into the region of 8.0 and then δ = 7.85 ppm. Its intensity relative to that of the butoxy-protons is 1 : 36.[14] The same signals have been recorded in the ^{1}H n.m.r. spectrum of bis-2-ethylhexyl hydrogen bis-2′-ethylhexyloxyphosphinoylimidophosphate (Fig.1*b*), but the corresponding intensity ratio is 1 : 68.

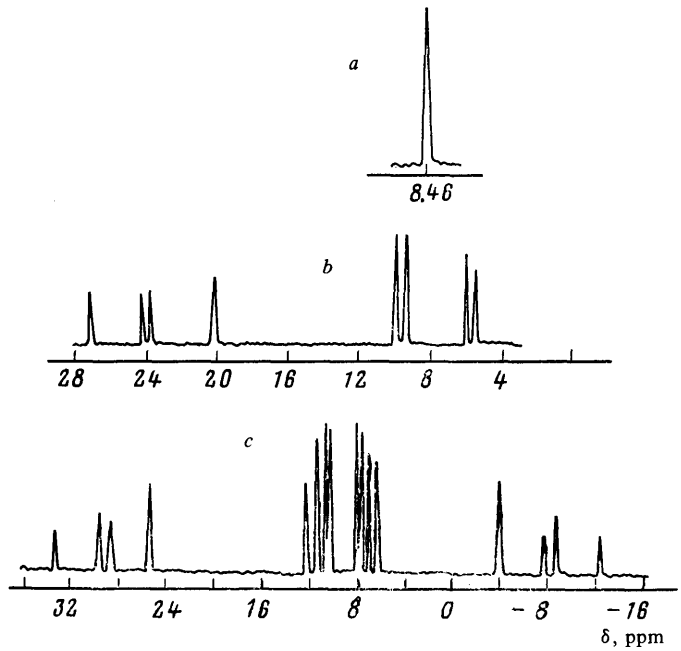


Figure 2. Spectra (^{31}P n.m.r.) of aryloxycyclotriphosphazens[102–104] of general formula $N_3P_3(OC_6H_4X)_5Y$ with X, Y: *a*) H, C_6H_5O; *b*) *p*-CH_3O, Cl; *c*) H, F.

Interesting information is provided by the ^{31}P n.m.r. spectra of aryloxycyclotriphosphazens (Fig.2).[102–104] Whereas those of the hexa-aryloxy-derivatives comprise a singlet with a chemical shift depending on the nature of the substituent in the phenoxy-groups (Fig.2*a*), the spectra of the penta-aryloxychlorocyclotriphosphazens were characteristic of an AB_2 system (Fig.2*b*), in which the A nucleus is the phosphorus atom attached to the chlorine atom, while the B nucleus is a phosphorus atom attached to two aryloxy-groups. The chemical shift of the phosphorus atom is determined by the surrounding distribution of electron density, but, despite the obvious dependence of the chemical shift of A on the character of the substituents in the phenoxy-groups, no correlation of δ_A and δ_B with their inductive constants σ is observed, apparently owing to a disregarded influence of substituents attached to the B nuclei[104].

The ^{19}F n.m.r. spectra of penta-aryloxyfluorocyclotriphosphazens[103], in which the fluorine atom is a magnetically active analogue of chlorine, contain two signals, corresponding to splitting on the nearest phosphorus atom, and represent an AB_2X system (Fig. 2c), in which A is the phosphorus atom combined with the fluorine atom, the B nuclei are phosphorus atoms attached to two aryloxy-groups, and X is the fluorine atom.

Investigation by n.m.r. spectroscopy of the structure of alkoxyphosphazens showed[105] that the chemical shift of the phosphorus atom bearing the substituent in the $N_3P_3Cl_5R$ molecule moves down-field in the sequence of substituents iso-C_3H_7O > C_2H_5O > CF_3CH_2O > CH_3O. The difference in chemical shifts between the fragments PClR and PCl_2 in the $N_3P_3Cl_5R$ molecule increases depending on the nature of R in the reverse sequence. Hence the action of the alkoxy-group in drawing electrons from the phosphorus atom promotes delocalisation of the lone pair on the ring nitrogen atom by displacing electron density towards the phosphorus atom.

Spin–spin coupling constants J depend on the substituents attached to each of the phosphorus atoms. Interaction of alkoxy-hydrogen atoms with the nearest phosphorus atom has been observed in the alkoxyphosphazen $N_3P_3X_5R$.[105,106]. Methylene protons in ethoxyphosphazens interact with a phosphorus atom, but the methyl protons, more remote from the phosphorus atom, do not usually interact with it[106]. Weak interaction between methyl protons and phosphorus-31 nuclei has been noted only in the geminal derivative $N_3P_3(C_6H_5)_4(OC_2H_5)_2$ (J = 0.8 Hz).[106]

IV. CHEMICAL PROPERTIES

Oligomeric alkoxyphosphazens are less reactive than chlorophosphazens. They are among the most stable phosphorus–nitrogen derivatives known. Within this group, however, thermal stability and resistance to hydrolysis largely depend on the nature of the alkoxy-group.

1. Nucleophilic Substitution

(a) Hydrolysis

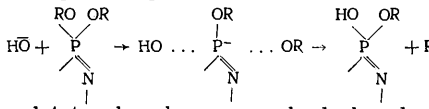
Trimeric and tetrameric alkoxyphosphazens $[NP(OR)_2]_n$ (R = CH_3, C_2H_5, iso-C_3H_7, C_4H_9; n = 3, 4) are not hydrolysed by water, but are decomposed by hot 10% hydrochloric acid. The corresponding benzyloxy-compounds behave similarly[33].

Fluoroalkoxyphosphazens $[NP(OCH_2CF_3)_2]_n$ (n = 3, 4) resist the action of concentrated hydrochloric and nitric acids, as well as aqueous alkalis[4,45], but undergo degradation in hot alcoholic alkalis. A detailed kinetic study of the alkaline hydrolysis of the series $[NP(OR)_2]_n$ (R = CF_3CH_2, $C_2F_5CH_2$, $C_3F_7CH_2$; n = 3, 4) showed[107] that under severe conditions (1 N alcoholic NaOH at 75 °C for 150 h) the compound $[NP(OCH_2CF_3)_2]_3$ forms the sodium salt of pentakistrifluoroethoxyhydroxycyclotriphosphazen. Increasing the duration of hydrolysis to 350 h yields the disodium salt of tetrakistrifluoroethoxydihydroxycyclotriphosphazen and the trisodium salt of tristrifluoroethoxytrihydroxycyclotriphosphazen. Under mild conditions (0.02 M NaOH in 25% aqueous diglyme at 80 °C for 24 h) the sodium salt of the monohydroxy-derivative is obtained[107,108]. Aryloxycyclophosphazens are hydrolysed similarly, those containing nitroaryloxy-groups especially readily[108].

A broad investigation of nucleophilic substitution in a series of aryloxyphosphazens $[NP(OAr)_2]_n$ (n = 3: Ar = p-ClC_6H_4, p-FC_6H_4, C_6F_5; n = 4: Ar = p-FC_6H_4, C_6H_5) studied[109] the action of sodium alkoxides, caesium fluoride, and potassium hydroxide in a polar solvent heated to 60–160 °C. It was assumed that the nucleophilic reagent replaced a phenoxy-group attached to a tetrahedral phosphorus atom in the phosphazen ring. The stability of the aryloxyphosphazens $(RO)_6N_3P_3$ to nucleophilic reagents diminishes in the sequence R = C_6H_5 > p-FC_6H_4 > p-ClC_6H_4 > p-$NO_2C_6H_4$ > m-$CF_3C_6H_4$ > C_6F_5. As the aryloxy-substituent becomes more acidic, the rate of nucleophilic substitution increases.

Alkaline hydrolysis of $(p\text{-}XC_6H_4O)_6N_3P_3$ (X = H, F, Cl) takes place under severe conditions (excess of alkali and moist diethylene glycol at 140–160 °C).[58] The resulting penta-aryloxycyclophosphazens $(p\text{-}XC_6H_4O)_5N_3P_3OH$ resist further hydrolysis. This is explained[58] by delocalisation of the negative charge of the anion over the phosphazen ring.

The rate of hydrolysis of alkoxycyclophosphazens increases with the electron-accepting power of the substituents. A tracer method has shown that hydrolytic cleavage takes place at a phosphorus–oxygen bond, not a carbon–oxygen bond. It has been suggested that hydrolysis takes place by an S_N2 mechanism with a five-coordinated trigonal–bipyramidal transition state[4]:



Alkoxycyclotetraphosphazens are hydrolysed considerably more rapidly than are the trimeric derivatives, as a consequence of the greater conformational freedom of the eight-membered ring[4].

Alkaline hydrolysis of spirocyclic alkoxyphosphazens containing five-membered exocycles involves detachment of aryloxy-groups followed by replacement of hydroxy-hydrogen atoms by sodium atoms[107,110]. The rate of detachment of the first group during the hydrolysis of compounds $N_3P_3(O_6H_4R)_6$ in 25% aqueous diglyme depends on the nature and position of the substituents R and decreases in the sequence p-NO_2 > m-NO_2 > o-NO_2 ≫ H > p-CH_3. The second aryloxy-group is removed from the phosphorus atom with greater difficulty than is the first: thus in the alkaline hydrolysis of $[(p\text{-}NO_2C_6H_4O)_2NP]_3$ at 80 °C the first group is eliminated within 25 min, but the second group not till the process has continued for 48 h.[110] The greater rate of hydrolysis of spirophosphazens containing five-membered exocycles was attributed to steric stress in the ring. When the phosphorus atom forms part of a six- or seven-membered exocyclic ring, steric effects increasing the rate of the first stage of hydrolysis are absent.

(b) Exchange of organic groups

The action of sodium trifluoroethoxide on hexa-p-nitrophenoxycyclotriphosphazen in oxolan forms either completely or partly substituted trifluoroethoxyphosphazens depending on the temperature[67,111]. The relative sequence in which different groups are replaced correlates approximately with their electronegativities. The p-nitrophenoxide ion is displaced by phenoxide, ethoxide, trifluoroethoxide, amide, and anilide ions, but not by n-propylamine, aniline, dimethylamine, and o-aminophenoxide ions. Ease of substitution varies in the sequence[67] o,p-$NO_2C_6H_4O$ > p-ClC_6H_4O ≥ C_6H_5O.

Treatment of $[(p\text{-}NO_2C_6H_4O)_2NP]_3$, $[(o\text{-}NO_2C_6H_4O)_2NP]_3$, and $[(CF_3CH_2O)_2NP]_n$ (n = 3, 4) with phenylmagnesium bromide and with methyl- and phenyl-lithium produces fission of the phosphazen ring with formation of linear products[4].

In the reaction of spirocyclophosphazens $[C_6H_4O_2NP]_3$, which contain five-membered exocyclic groups, with the trifluoroethoxide ion and with n-propylamine, diethylamine, and piperidine one aryloxy-group is substituted on each phosphorus atom. Spirocyclophosphazens containing seven-membered exocycles, e.g. $[C_{12}H_8O_2NP]_3$, do not undergo such reactions[4].

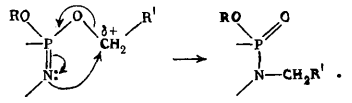
2. Electrophilic Substitution

Little published information is available on the electrophilic substitution of alkoxyphosphazens. Chlorination of the fluoroalkoxyphosphazens $N_3P_3(OCH_2C_3F_7)_6$, $N_3P_3.(OCH_2C_2F_5)_{6,8}$, and $[NP(OCH_2[CF_2]_9CF_2H_2)]_4$ on ultraviolet exposure in tetrachloromethane for 72 h has been described[4]; α-chlorofluoroalkoxy-derivatives are formed.

The nitration, chlorination, and bromination of hexaphenoxycyclotriphosphazen have been studied[109]. Nitration is effected with a mixture of sulphuric and nitric acids at 25 °C for 4–5 h. Chlorination was accomplished with chlorine in acetic acid at 25 °C for 25 h, or in the melt in the presence of iodine at 110–120 °C for 5 h. Bromination was carried out similarly. Only *para*-substituted aryloxycyclophosphazens were formed. Further substitution in an *ortho*-position took place only under severe conditions; *meta*-substitution was not observed. Preferential *para*-orientation was attributed[109] to electronic and steric effects. Electrophilic substitution of aryloxyphosphazens takes place under more severe conditions than for the corresponding reactions of aryl phosphates, cyanurates, and carboxylates.

3. Rearrangement of Alkoxyphosphazens into Oxophosphazans

With rise in temperature hexa-alkoxyphosphazens undergo what has been termed the phosphazen–phosphazan rearrangement[112–114]:

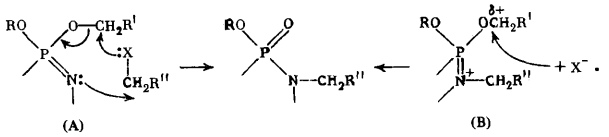


The process could occur either intramolecularly or intermolecularly, the latter being regarded as the more probable[112]. Thus when hexaethoxycyclotriphosphazen (a colourless liquid) is heated at 200 °C for 1 h, it passes into 2,4,6-triethoxy-1,3,5-triethyl-2,4,6-trioxocyclotriphosphazan (a white solid). Heating the corresponding tetramer at 200 °C for 4 h also results in formation of a phosphazan.

The same rearrangements have been noted when $[NP(OCH_3)_2]_{3,4}$ [113–115] and $[NP(OCH_2C_6H_5)_2]_3$ [112] are heated. Nevertheless, aryloxy- and perfluoroalkoxy-cyclophosphazens $[NP(OC_6H_5)_2]_{3,4}$ and $[NP(OCH_2CF_3)_2]_{3,4}$ do not undergo rearrangement even on prolonged heating at 300 °C.[4] Benzyloxycyclophosphazens $[NP(OCH_2C_6H_5)_2]_4$ occupy an intermediate position. Rearrangement is supposed[4] to be due to nucleophilic attack by the ring nitrogen atom on the α-carbon atom of the alkoxy-group. Thus ease of rearrangement depends on the basicity of the cyclic nitrogen atoms. Trifluoroethoxy- and phenoxy-groups tend to attract electrons from phosphorus and nitrogen atoms, thus lowering the basicity of the skeletal nitrogen atom and retarding nucleophilic attack (attack by nitrogen atoms on aromatic carbon is especially difficult).

The phosphazen–phosphazan rearrangement of hexamethoxycyclotriphosphazen and octamethoxycyclotetraphosphazen has been investigated by ^{13}C and ^{31}P n.m.r. spectroscopy at 140–160 °C.[115] Significant changes in the carbon-13 spectrum during rearrangement have enabled the kinetics to be assessed, the stages to be followed (rearrangement at one, two, or all three cyclic phosphorus atoms), and also the isomeric composition of the resulting cyclophosphazens to be determined. Rearrangement of octamethoxycyclotetraphosphazen produces only one of the three possible stereoisomers; subsequent heating at 160 °C for 24 h yields a second isomer. Rearrangement of both trimeric and tetrameric polymethoxycyclophosphazens is autocatalytic, with respective activation energies 134 and 133.6–144.4 kJ mole^{-1}.[115]

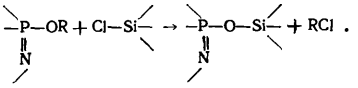
The rearrangement is accelerated by alkyl halides, additions of which lower the reaction temperature and increase the yield of phosphazans[116,117]. Since a cyclic nitrogen atom possesses increased electron density, rearrangement may involve either a six-membered transition state (A) or a quaternary compound (B), with subsequent nucleophilic attack by the halide ion on the α-carbon atom:



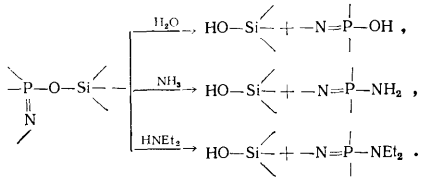
Several new compounds could be obtained by the use, as initiators of phosphazen–phosphazan rearrangement, of alkyl or aryl halides whose radicals differed in structure from the alkoxy-group in the initial phosphazen[117]. Thus isopropyl iodide reacts with hexaethoxycyclotriphosphazen to give an oxophosphazan containing *N*-isopropyl groups. *p*-Nitrobenzyl bromide reacts similarly. With the hexamethoxy-compound benzyl bromide yields a product containing only two benzyl groups. Partly rearranged alkoxycyclophosphazens have also been prepared[118], e.g. 2,2,4,4,6-pentaethoxy-5-ethyl-6-oxocyclotriphosphazo-1,3-dien. Bulky alkoxy-radicals in the phosphazen or in the alkyl halide hinder or completely inhibit rearrangement.

4. Action of Chlorosilanes and Alkylchlorosilanes on Alkoxyphosphazens

Investigation of the reactions between alkoxyphosphazens and halogenosilanes, leading to the formation of siloxyphosphazens containing P–O–Si and P–O–C–Si links[78,119–127], has provided new information on the transmission of inductive effects in molecules and opens up wide possibilities for the synthesis of difficultly accessible alkoxyphosphazen derivatives and also silicon-containing polyphosphazens. Oligomeric alkoxyphosphazens are fairly inert chemically, so that examination of the action of chlorosilanes was a convenient method for elucidating the structural dependence of the reactivity of the former:



The alkoxy-siloxyphosphazens were identified by infrared and n.m.r. (^{31}P and ^{1}H) spectroscopy, as well as by their reactions[122-124]



These processes confirmed the phosphazen (not phosphazan) structure of the products.

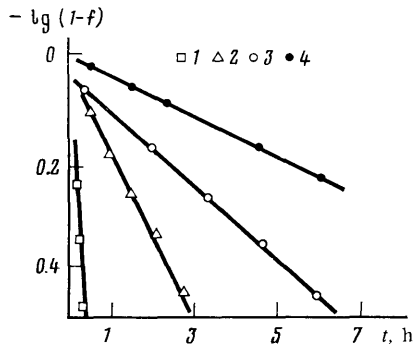


Figure 3. Variation with time of degree of conversion f in nitridobisdialkoxophosphorioamidophosphates[120,121] $HO[P(OR)_2{:}N]_3PO(OR)_2$ with R: *1*) n-C_4H_9; *2*) iso-C_4H_9; *3*) $CH_3OC_2H_4$; *4*) ClC_2H_4.

The reactions of halogenosilanes with alkoxyphosphazens are greatly influenced by the structure of the latter. Linear alkoxyphosphazens react with chlorosilanes even at 90–100 °C. The reaction has overall first order (Fig. 3), zero with respect to the chlorosilane and first with respect to the phosphazen[120,121]. With increase in chain length of the alkoxyphosphazen the rate constant undergoes extremal variation, passing through a maximum for dialkoxophosphoriobisamidophosphates and then decreasing monotonically with increase in the number of phosphorus and nitrogen atoms in the molecule (Table 5). Imidobisphosphoric and dialkoxophosphoriobisamidophosphoric esters exhibit linearity of free energies, and the rate constants of their reactions with chlorosilanes correlate with the sum of the inductive constants of the hydrocarbon substituents

$$\left(\sum \sigma^* = \sigma^*_{R'} + 2\sigma^*_H\right)$$

and the Kabachnik constants σ_{ph}, but such correlation is not observed for subsequent linear alkoxyphosphazen homologues. The reason is the complication of their structure and the progress of reactions at different rates (replacement of alkoxy-groups at outer and inner phosphorus atoms, as well as at a phosphorus atom already attached to a siloxy-group). The rate constant varies little with the nature of the alkoxychlorosilane. Table 5 lists rate constants and activation energies for the reaction between linear alkoxyphosphazens and chlorosilanes.

Cyclic alkoxyphosphazens react at an appreciable rate with chlorosilanes above 120 °C. The overall kinetic order is maintained, but the partial orders—zero with respect to phosphazen and first with respect to chlorosilane—are different[122-124]. On passing from hexafunctional alkoxycyclophosphazens to derivatives containing a smaller number of cyclic alkoxy-groups the reaction velocity drops appreciably, this being especially marked with alkoxypentaaryloxycyclotriphosphazens, which react with chlorosilanes only above 190 °C. The reactivity of the chlorosilanes used diminishes with increase in the number of phenyl groups attached to the silicon atom.

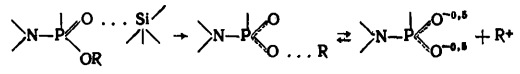
Table 5. Kinetic parameters (rate constant k and activation energy E) for the action of equimolecular proportions of chlorosilanes and chloroalkylsilanes on linear, cyclic, and cyclolinear alkoxyphosphazens $HOP(OR)_2{:}NPO(OR)_2$, $(RO)_5P_3N_3OC_4H_9$, and $(RO)_4P_3N_3$. $.[N{:}P(OR)_2OH)_2$.[120-125]

Silane	R	T, °C	$10^{-2}k$, min^{-1}	E, kJ mole^{-1}
linear alkoxyphosphazens				
Ph_3SiCl	iso-C_4H_9	100	1.78	—
Ph_3SiCl	iso-C_4H_9	110	4.15	99.7
Ph_3SiCl	iso-C_4H_9	120	8.75	—
Ph_3SiCl	C_2H_4Cl	110	1.07	—
Ph_3SiCl	C_2H_4Cl	120	2.48	106.4
Ph_3SiCl	C_2H_4Cl	130	5.46	—
cyclic alkoxyphosphazens				
$Me_2PhSiCl$	n-C_4H_9	120	10.50	—
$Me_2PhSiCl$	n-C_4H_9	130	25.50	103.9
$Me_2PhSiCl$	n-C_4H_9	140	47.20	—
$Me_2PhSiCl$	n-C_4H_9	140	16.90	—
Ph_3SiCl	n-C_4H_9	140	7.60	—
Ph_3SiCl	Ph	190	0.41	—
$ClCH_2Si(OBu)_3$	Ph	160	2.57	—
$ClCH_2SiMe(OBu)_2$	Ph	160	1.54	108.9
$ClCH_2SiMe(OBu)_2$	Ph	170	2.36	108.9
$ClCH_2SiMe(OBu)_2$	Ph	180	3.23	108.9
$ClCH_2SiMe_2Ph$	Ph	160	1.08	—
cyclolinear alkoxyphazens				
Ph_3SiCl	n-C_4H_9	100	0.95	—
Ph_3SiCl	n-C_4H_9	110	2.29	99.7
Ph_3SiCl	n-C_4H_9	120	5.01	—
Ph_3SiCl	iso-C_4H_9	100	1.25	—
Ph_3SiCl	iso-C_4H_9	110	2.63	86.7
Ph_3SiCl	iso-C_4H_9	120	5.28	—
Ph_3SiCl	$C_2H_4OCH_3$	100	0.75	—
Ph_3SiCl	C_2H_4Cl	100	0.40	—

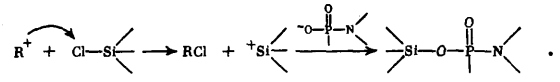
Cyclolinear alkoxyphosphazens also react with alkylchlorosilanes by a first-order mechanism under conditions closely similar to those for linear phosphazens, and with the same partial kinetic orders, which indicates substitution of alkoxy-radicals in exocyclic phosphazo-groups. However, replacement of alkoxy- by siloxy-groups takes place more slowly than in linear alkoxyphosphazens (Table 5), an effect of the phosphazen ring[78]. Yet activation energies are close to the corresponding values for linear alkoxyphosphazens. Rate constants for the reactions of cyclolinear alkoxyphosphazens with chlorosilanes do not correlate with the Kabachnik constants. As in the case of the ionisation constants of cyclolinear alkoxyphosphazens, these facts indicate absence of conjugation between exocyclic phosphazo-groups and the phosphazen ring.

Kinetic study of the action of alkylchlorosilanes on alkoxyphosphazens varying in molecular structure (Table 5), together with examination of starting materials and reaction mixtures at various stages by infrared, ultraviolet, and

n.m.r. spectroscopy, suggested heterolytic mechanisms[76, 120–122]. In the case of linear and cyclolinear alkoxyphosphazens the initial compounds form an intermediate complex by coordination of the silicon atom with a phosphoryl group. Such coordination facilitates ionisation of the P–O–C link and formation of a carbocation

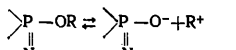
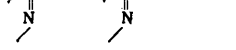
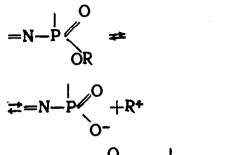
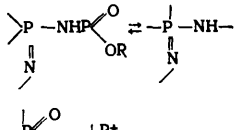


which is responsible for subsequent rapid reactions



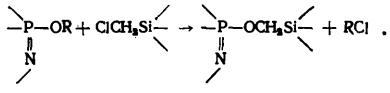
The rate-determining stage in the overall unimolecular interaction of cyclic alkoxyphosphazens and alkylchlorosilanes is ionisation of the $\equiv$Si–Cl bond, which is followed by rapid attack by the siliconium cation on the oxygen atom in the P–O–C bond. Ionisation mechanisms of these reactions are due to the nature of the reactants involved: both alkylchlorosilanes and alkoxyphosphazens contain polar bonds of electropositive elements (phosphorus and silicon), which facilitates heterolytic processes.

Table 6. Comparative data for the reactions of alkoxyphosphazens with chlorosilanes and chloromethylsilanes[78,119–127].

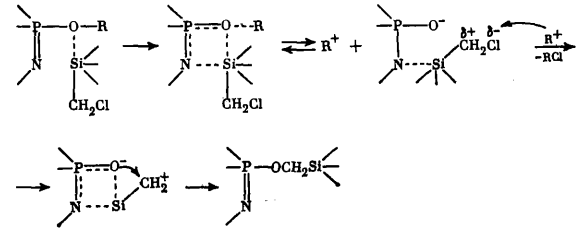
Alkoxyphosphazens	Silanes	T_{min}, °C	Kinetic order* N_Σ	N_{Ph}	N_{Si}	E, kJ mole^{-1}	Slow stage
Cyclic	$\equiv$Si–Cl	120	1	0	1	62.9–104.8	
Cyclic	$\equiv$SiCH$_2$Cl	160	1	1	0	104.8	
Linear	$\equiv$Si–Cl	90	1	1	0	83.8–113.1	
Cyclolinear	$\equiv$Si–Cl	100	1	1	0	83.8–96.4	

*Order of reaction–overall N_Σ, with respect to phosphazen N_{Ph}, and with respect to silane N_{Si}.

Additional confirmation of the validity of the proposed mechanisms was obtained by studying the reaction between alkoxyphosphazens and chloromethylsilanes[125–127]:



The introduction of a methylene group between silicon and chlorine atoms produces sharp changes in the reaction conditions and characteristics: with both linear and cyclic alkoxyphosphazens reaction takes place above 150 °C, in both cases first order with respect to the phosphazen and zero order with respect to the silane (Table 6). Obviously here, too, heterolytic fission of the P–O–C link is involved followed by rapid reactions of the resulting carbocation. As in the action of chlorosilanes on alkoxyphosphazens, formation of the carbocation is facilitated by donor–acceptor interaction between the initial molecules, in particular coordination of the silicon atom with oxygen and nitrogen atoms of the alkoxyphosphazen. The mechanism



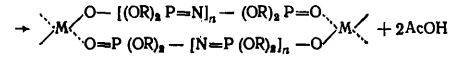
has been suggested[27] as the most probable for the action of choromethylsilanes on alkoxyphosphazens.

Thus all these reactions are characterised by the heterolytic nature of their slow stages.

5. Alkoxy- and Aryloxy-phosphazens in Polymer Formation

(*a*) Polymers based on linear alkoxyphosphazens

A new type of polymer—coordinated polyphosphazens—has been obtained[128] by the interaction of linear alkoxyphosphazens with compounds of transition metals:



Dibutyl hydrogen dibutoxyphosphinoylimidophosphate and tetrabutyl hydrogen nitrodobisdibutoxyphosphorioamidophosphate have been used as initial alkoxyphosphazens; the transition-metal salts were zinc and cobalt acetates. Reaction was conducted in the absence of a solvent or in anhydrous ethanol at 60 °C. The ratio of phosphazen and phosphazan bonds in the macromolecule can be changed by varying the process conditions.

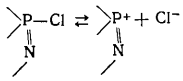
The resulting coordinated polyalkoxyphosphazen polymers have comparatively low thermal stability, but the very fact of their formation has great value, and can be used to diminish the tendency of linear polydialkoxyphosphazens to depolymerise, by blocking their terminal groups (P–OH and P=O).

(*b*) Polymers based on cyclic alkoxyphosphazens

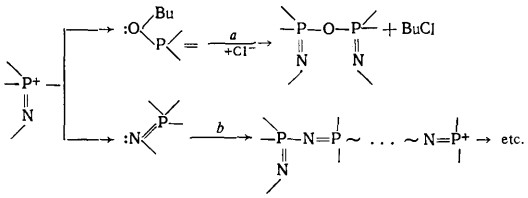
Most of the numerous attempts to accomplish the thermal and catalytic polymerisation of alkoxyphosphazens have been unsuccessful. Thus hexaphenoxycyclotriphosphazen withstands prolonged heating at 350 °C without polymerising[129]. In the presence of acid catalysts at temperatures up to 300 °C hexa-aryloxycyclotriphosphazens undergo oligomerisation with an insignificant yield of macromolecular compounds. N-Propoxy-, n-butoxy-, and cyclohexoxy-derivatives do not polymerise when heated in

the presence of benzoyl peroxide or aluminium chloride to 350 °C.[130] Fluoroalkoxycyclophosphazens $[NP(OCH_2R_F)_2]_n$ ($R_F = CF_3$, C_2F_5, C_3F_7; $n = 3, 4$) do not polymerise on prolonged heating at 250–300 °C.[4] An attempt[131] to obtain a linear polymer $[(C_6F_5O)_2PN]_n$ by heating gave a contaminated insoluble product. Incompletely substituted penta-, tetra-, and tri-chlorofluoroalkoxy-, as well as pentachloro-phenoxy-, pentachloro-*p*-halogenophenoxy-, and pentachloro-*p*-methoxyphenyl-phosphazens can be polymerised at temperatures not below 250 °C.[132–134]. Hexakistrifluoroethoxycyclotriphosphazen copolymerises with hexachlorocyclotriphosphazen when heated to 200 °C.[132,133]

When tetrabutoxydichloro- and pentabutoxychloro-cyclotriphosphazens are heated in the absence of a catalyst in the melt or in a polar solvent at 150–200 °C, polymers are formed in which phosphazen rings are linked by P–O–P bonds[135]. The infrared spectra show that polycondensation is accompanied by partial polymerisation of butoxyphosphazen rings, with consequent inclusion of linear butoxyphosphazen fragments in the macromolecules. The rate-determining stage is ionisation of a phosphorus–chlorine bond



followed by rapid attack by the cyclic azophosphonium cation on the oxygen atom in a P–O–C link (path *a*) or on a cyclic nitrogen atom (path *b*)—nucleophilic centres of the butoxyphosphazen molecules



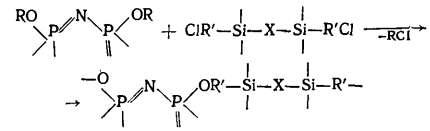
The presence of linear phosphazen fragments in the polymer macromolecules indicates that nitrogen atoms are more accessible to nucleophilic attack in butoxyphosphazen rings than in hexa-aryloxyphosphazens. An important role is played by steric effects and also the more strongly electron-donor character of butyl groups. Weakening of the nucleophilic character of the oxygen atoms in P–O–C links, e.g. in chloroperfluoroalkoxycyclotriphosphazens, increases the proportion of reactions following path *b*; this applies also to substituents that increase the electron density in the phosphazen ring.

(*c*) Alkoxyphosphazens containing spirocyclic groups at phosphorus atoms

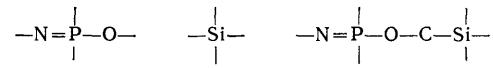
These compounds are capable of thermal polymerisation. For example, tripyrocatecholcyclotriphosphazen polymerises with opening of the phosphazen ring when heated above 250 °C.[136] However, related compounds having six- and seven-membered exocycles containing the phosphorus atom do not undergo thermal polymerisation, owing to repulsion of substituents in the polymer consequent on the large angle of rotation of biphenyl groups from the plane of the phosphazen ring[137].

(*d*) Synthesis of polyphosphazens containing silicon and boron

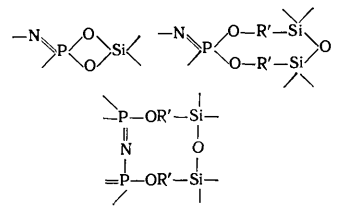
Phosphazen polymers containing silicon and boron are attracting increasing attention from research workers by virtue of their great thermal stability, resistance to radiation, and other valuable properties. Silicon-containing polyphosphazens have been obtained by the polycondensation of alkoxyphosphazens and organosilicon compounds[138,139]:



where R = Alk (e.g. n-C_4H_9); R′ = –, CH_2, $[CH_2]_3$; X = O, $[O.SiH_2]_n$. In the course of the reactions polyphosphazens containing the links



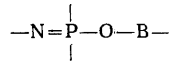
were obtained. A characteristic feature of the polycondensations is that spiran structures such as



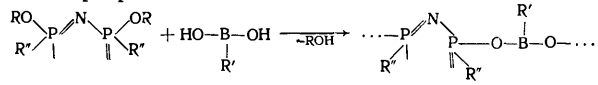
may be formed within the macromolecules.

Under otherwise similar conditions the most active among several initial butoxyphosphazens is the cyclic hexabutoxy-derivative; mixtures of oligomeric butoxyphosphazens in which the hexabutoxyphosphazen predominates are somewhat less reactive, as are also linear butoxyphosphazens, which is due to stabilisation of their functional groups by complex formation. The activity of chloromethylsiloxanes is determined by their molecular structure and the number of functional groups. Cyclic chloromethylsiloxanes or their mixtures with linear siloxanes are more reactive. In all cases investigated the process is first order (partial first order with respect to the phosphazen and zero order with respect to the siloxane) during the initial stages of polycondensation. The mechanism of polycondensation is analogous to that suggested for simple model compounds.

Boron-containing phosphazen polymers containing the links

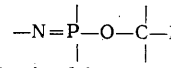


have been prepared[140]:

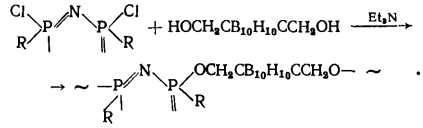


R=Me, Bu; R′=OH, Bu, Ph; R″=Cl, OPh .

Those containing

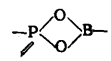


links have been obtained by the polycondensation of alkoxyphosphazens and carboranediols[141]:



The reaction was conducted in the melt or in an inert solvent at temperatures up to 150 °C.[141]

As with silicon-containing polyphosphazens, heterolytic processes have a decisive role in the formation of polymers containing boron and phosphorus. A characteristic feature of the polycondensation is a well defined tendency to cyclisation and the inclusion of spirocyclic fragments



in the macromolecules. Polyphosphazens containing P–O–C–Si and P–O–C–B links possess good hydrolytic stability. The strength of the P–O–Si and P–O–B bonds can be enhanced significantly by attaching to the phosphorus, silicon, and boron atoms bulky substituents, which also lower the nucleophilicity of these atoms.

V. APPLICATIONS

The practical value of alkoxyphosphazens and polymers based on them is due to a number of specific properties—heat resistance, non-flammability, possibility of obtaining hyperelastic and hard materials having good mechanical and dielectric parameters, high chemical and radiation resistance, etc.

Alkoxycyclophosphazens are finding increasing application as high-temperature (up to 500 °C) heat-transfer agents, lubricating and transformer oils, hydraulic liquids having low solidification temperatures, and heat-resistant plasticisers. Aryloxy- and fluoroalkoxy-phosphazens are characterised by enhanced heat resistance[142–146]. They are distinguished by high chemical and thermal stability, high flash-points, low vapour pressures, and good lubricating properties; they do not cause metallic corrosion.

Including phenoxyhalogenophosphazens in the composition improves the flame-resistance of polyesters[147,148]; flame-resistant materials have been obtained by impregnating wool, cotton, polyamide, viscose, and polyurethane fibres and fabrics with fluoroalkoxy- and halogenophenoxy-phosphazens[149–157]. Pentakistetrafluoropropoxycyclotriphosphazen can be used as a modifying agent for phenol–formaldehyde resins[158]. Flame-resistant water-soluble liquids and greases can be based on aminophenoxyalkene oxide adducts of cyclophosphazens[159].

Introduction of alkoxycyclotriphosphazens into mineral oils not only enhances their heat and flame resistance but also diminishes the wear of rubbing components: thus additions of 0.7–3.0 mass % decrease wear by 20–40%, ethers of lower alcohols being the more effective[160]. Geminal difluorotetramethoxycyclotriphosphazens can be used as insecticides[161]. Hydroxy-derivatives of alkoxy-, amino-, and alkoxyamino-cyclotriphosphazens are strong complexing agents and have been used for the extraction of plutonium, neptunium, uranium, and platinum from aqueous solutions[162,163].

A promising use of alkoxyphosphazens is the preparation of various types of polymers. Thus novel silicon-containing phosphazen polymers can be used as dressings in the production of glass plastics[164]. In mechanical properties the products equal those obtained industrially with KM-9K organosilicon dressing, but surpass them in dielectric properties, especially at high temperatures.

Even this brief list of possible practical applications of alkoxyphosphazens reveals their great value for various branches of technology and the undoubted promise of further research on these lines.

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